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Contributions from the Sheffield Laboratory of Yale University.

CVIII.—ON SOME PSEUDODITHIOBIURETS.

BY TREAT BALDWIN JOHNSON.

The non-substituted pseudothioureas,

$$NH=C(SR)—NH_2 (R=CH_3—, C_2H_5—),$$

have received very little attention. It is only recently that they have been found to be capable of isolation. In some previous papers from this laboratory[1] it has been shown that the free pseudothioureas are not so unstable as one would be led to believe, and it has been found that they can be isolated from their halide salts at low temperatures.

The work described in this paper was undertaken at the suggestion of Prof. H. L. Wheeler, with the object of investigating the action of isothiocyanates on these simple pseudothioureas, and also some of the type

$$RN=C(SR')—NH_2 (R=C_6H_5, C_7H_7—).$$

I find that the non-substituted pseudothioureas are fairly stable in aqueous solution at ordinary temperature, and combine very smoothly with isothiocyanates, giving a new class of pseudodithiobiurets.

The first pseudodithiobiurets were prepared by Tursini[2] by

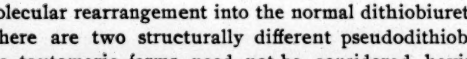
[1] This JOURNAL, 29, 478, 492 (1903).

[2] Ber. d. chem. Ges., 17, 585.

treating phenyldithiobiuret and paratolyldithiobiuret with ethyl iodide in the presence of ammonia. He also mentions the corresponding pseudomethyl derivatives. Tursini showed that the alkyl radical was joined to sulphur, but did not determine to which sulphur atom it had attached itself.

Billeter[1] has described a somewhat different type of pseudodithiobiurets, which he obtained by treating certain thioureas with thiocarbamic chlorides. He furthermore made the interesting observation that his pseudodithiobiurets underwent a molecular rearrangement into the normal dithiobiurets.

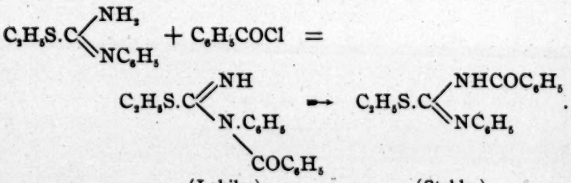
There are two structurally different pseudodithiobiurets, since tautomeric forms need not be considered, having the composition of Tursini's phenyl derivative:



I. II.

We have prepared the pseudoethyldithiobiuret (Formula II.) by treating pseudoethylthiourea with phenyl isothiocyanate. We find that it does not agree in any of its properties with Tursini's body. Tursini's pseudoethyldithiobiuret must, therefore, be the isomeric substance having the structure shown in Formula I.

In a previous paper[2] from this laboratory it has been shown that when a substituted pseudothiourea is treated in the cold with an acid chloride that the acyl radical first attacks the nitrogen atom which is joined to the aryl group. An unstable acyl derivative is formed, which very easily undergoes a molecular rearrangement into a stable isomer.



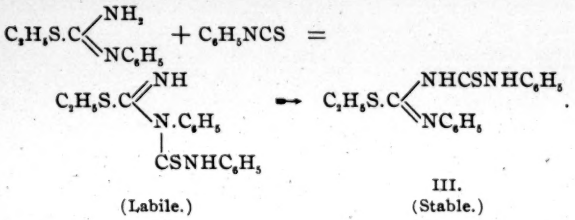
(Labile.) (Stable.)

[1] *Ibid.*, **31**, 108; **36**, 1688.

[2] This JOURNAL, **27**, 270 (1902).

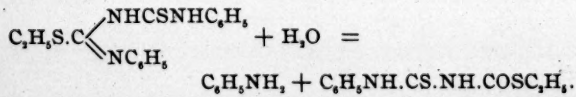
Busch and Holzmann[1] made a similar observation in the action of isothiocyanates on phenylhydrazine. Contrary to the rule of stereochemical interference, it was the nitrogen atom attached to the phenyl group which was the first point of attack by the isothiocyanate. Labile products were obtained which underwent a metastatic change into symmetrical thiosemicarbazides.

It might be expected, like the above, that when an isothiocyanate is allowed to act on a substituted pseudothiourea an analogous reaction would take place; that a labile product would first be formed, which would undergo a molecular rearrangement into a stable isomer:



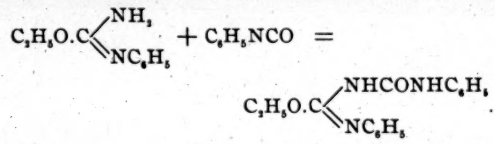
(Labile.) III. (Stable.)

We find that isothiocyanates react with the aromatic substituted pseudothioureas with extreme smoothness. They react best at ordinary temperatures and yield quantitatively pseudodithiobiurets. With the various pseudothioureas, which we have examined, we have not observed the formation of any labile products. The isothiocyanate unites with the amino radical of the pseudothiourea in preference to the nitrogen which is attached to the aryl group. The structure of the pseudodithiobiurets is shown in Formula III., since on hydrolysis they decompose as represented in the following equation:

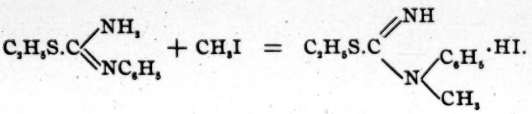


[1] Ber. d. chem. Ges., **34**, 320 (1901).

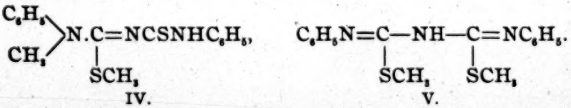
Our results are perfectly analogous to those of McKee,[1] who described the behavior of phenyl isocyanate towards the oxygen pseudoureas :



Bertram[2] has shown that when phenylthiolmethylpseudothiourea is treated with a molecular proportion of methyl iodide, that the methyl radical attaches itself to the nitrogen atom which is joined to phenyl :



Theoretically, an analogous addition might be expected to take place by treating our pseudodithiobiurets with methyl iodide (Formula IV.), or the methyl radical would attach itself to sulphur, giving a dipseudodithiobiuret (Formula V.).



IV. V.

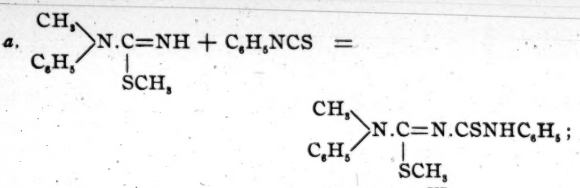
We find that our pseudodithiobiurets add on methyl iodide very smoothly, giving products which are well crystallized and easy of purification. That the alkyl radicals in these addition-bodies are attached to sulphur and not to nitrogen is proved by the following experiments :

I. When *a*-phenyl-*a*-methylthiolmethylpseudothiourea is treated with phenyl isothiocyanate a different biuret is ob-

[1] This JOURNAL, **26**, 209 (1901).
[2] Ber. d. chem. Ges., **25**, 52.

tained than when methyl iodide is added to *a*,*c*-diphenyl-1-thiolmethylpseudodithiobiuret :[1]

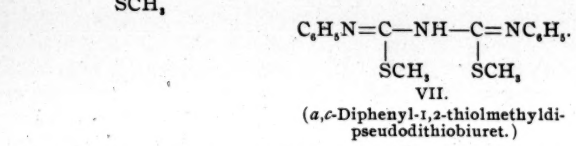
a.



VI.

(*a*,*c*-Diphenyl-*a*-methyl-1-thiolmethylpseudodithiobiuret.)

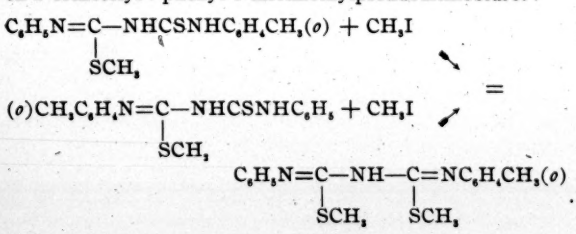
b.



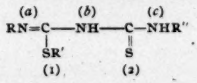
VII.

(*a*,*c*-Diphenyl-1,2-thiolmethyldipseudodithiobiuret.)

II. The same dipseudodithiobiuret results when *a*-phenyl-*c*-orthotolyl-1-thiolmethylpseudodithiobiuret is treated with methyl iodide, as is obtained by the action of methyl iodide on *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret :



[1] In the dithiobiurets the nitrogen atoms will be designated alphabetically—*a*, *b*, *c*—; The sulphur atoms will be designated numerically—1, 2—:



It has been shown in previous papers from this laboratory[1] that when two of the radicals—S.alk—, O.alk—, CO—, CS— are present in certain compounds, that they react with the amino hydrogen of phenylhydrazine in the following order:

$$-S.R > -CS > -CO > -OR.$$

Our pseudodithiobiuret seemed suitable for making a further test of this law, since both a mercapto and a thion grouping are present. We found, however, that our dithiobiurets reacted abnormally with phenylhydrazine. Instead of reacting to give triazole derivatives the phenylhydrazine simply removed the mustard oil from the pseudodithiobiuret, forming diphenylthiosemicarbazide.

EXPERIMENTAL PART.

By Howard S. Bristol.

a-Phenyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHCSNH_2$.—This pseudodithiobiuret has previously been mentioned by Tursini,[2] but he did not describe its properties or give the melting-point of the body. We prepared it according to Tursini's directions by treating phenyldithiobiuret with methyl iodide in the presence of ammonia. It crystallized from alcohol in long prisms and melted at 122°. A nitrogen determination gave:

	Calculated for $C_9H_{11}N_3S_2$.	Found.
N	18.66	18.20

a-Phenyl-2-thiolmethylpseudodithiobiuret, $C_6H_5NHCSNHC(SCH_3){=}NH$. — This pseudodithiobiuret was obtained by allowing phenyl isothiocyanate to act at ordinary temperature on thiolmethylpseudothiourea. The methyl iodide addition-product of thiourea was dissolved in the least possible quantity of water and the free pseudothiourea precipitated with one molecular proportion of potassium hydroxide. To this aqueous solution of the free base was added a molecular proportion of phenyl isothiocyanate. The mixture was then allowed to stand, with occasional shaking,

[1] This Journal, **27**, 258 (1902); **29**, 73 (1903).
[2] *Loc. cit.*

for twelve hours at ordinary laboratory temperature. A white solid separated in the form of balls, which was purified by crystallizing from alcohol. It separated in the form of prisms and melted with effervesence at 124°. When it was mixed with the above pseudodithiobiuret of Tursini's, melting at 122°, the melting-point was lowered to 102°. A nitrogen determination gave:

	Calculated for $C_5H_{11}N_3S_2$.	Found. I.	Found. II.
N	18.66	18.53	18.56

When this pseudothiobiuret was boiled in alcoholic solution with phenylhydrazine, phenyl isothiocyanate was split off, yielding diphenylthiosemicarbazide melting at 176°. When mixed with pure diphenylthiosemicarbazide the melting-point was not changed.

a-Phenyl-2-thiolethylpseudodithiobiuret, $C_6H_5NHCSNHC(SC_2H_5)=NH$.—This dithiobiuret was obtained by allowing phenyl isothiocyanate to combine with thiolethylpseudothiourea. The method of procedure was the same as in the preceding preparation of the methyl derivatives. A yellow solid was obtained which separated from dilute alcohol in the form of tables and melted at 114°. The yield was quantitative. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}N_3S_2$.	Found.
N	17.57	17.46

Paratolylthiolmethylpseudothiourea, $(p)CH_3C_6H_4N=C(SCH_3)NH_2$.—This pseudothiourea has recently been described as an oil by Dixon,[1] who obtained it by the action of methyl chlorformate on paratolylthiourea. We have obtained the same pseudothiourea in the form of its hydriodide by warming on the steam-bath paratolylthiourea (moistened with alcohol) with a slight excess of methyl iodide. The hydriodide was obtained in the form of microscopic prisms, and after crystallization from a mixture of alcohol and ether it melted with effervescence at 129° to 130°. The free base was obtained by neutralizing an alcoholic solu-

[1] J. Chem. Soc. (London), 83, 556 (1903).

tion of the hydriodide with sodium carbonate. It was exceedingly soluble in alcohol and was reprecipitated by water as an oil which solidified on long standing. It crystallized from petroleum ether in plates and melted at 65° to 67°. A nitrogen determination in the free pseudothiourea gave :

	Calculated for $C_9H_{12}N_2S$.	Found.
N	15.50	15.60

The hydriodide was analyzed with the following result :

	Calculated for $C_9H_{13}N_2SI$.	Found. I.	Found. II.
N	9.09	9.41	9.25

a-Paratolyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(p)CH_3C_6H_4N{=}C(SCH_3)NHCSNHC_6H_5$. — This was obtained by allowing phenyl isothiocyanate to act for several hours at ordinary temperature on paratolylthiolmethylpseudothiourea, which had previously been dissolved in ether. By spontaneous evaporation of the ether, a crystalline body was obtained, which crystallized from alcohol in prisms and melted at 93°. It was very soluble in ether and warm alcohol, but insoluble in benzene and petroleum ether. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found. I.	Found. II.
N	13.33	13.18	13.20

When this dithiobiuret was boiled in alcoholic solution with a molecular proportion of phenylhydrazine, a slow reaction took place with formation of diphenylthiosemicarbazide. It melted at 174° to 175° with effervescence, and a nitrogen determination gave :

	Calculated for $C_{13}H_{13}N_3S$.	Found.
N	17.29	17.60

a-Paratolyl-c-phenyl-1,2-thiolmethyldipseudodithiobiuret, $(p)CH_3C_6H_4N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5$. —— When *a*-paratolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret was treated in alcohol with a molecular proportion of methyl iodide a slow reaction took place with evolution of heat. After stand-

ing a few hours, beautiful, colorless prisms separated which melted, after several crystallizations from alcohol, at 164° with effervescence. A nitrogen determination agreed with the calculated for a methyl iodide addition-product. This hydriodide was rather difficultly soluble in water, but very soluble in warm alcohol. The free base was obtained by treating an alcoholic solution of the hydriodide with aqueous ammonia. It was precipitated as an oil, which showed no signs of solidifying after standing in an open dish for six weeks. A nitrogen determination in the hydriodide gave :

	Calculated for $C_{11}H_{19}N_3S_2.HI$.	Found.
N	9.19	9.39

a-Paratolyl-a-methylthiolmethylpseudothiourea, $(CH_3)(C_7H_7)N.C(SCH_3)=NH$.—This pseudourea was obtained in the form of its hydriodide by allowing methyl iodide to act on paratolylthiolmethylpseudothiourea. The reaction takes place with such violence that it is necessary to use a condenser. The methyl iodide addition-product was purified by crystallizing from a mixture of alcohol and ether, and it melted at 190° to 191° with effervescence. The free base was obtained as an oil by neutralizing an aqueous solution of the hydriodide with sodium carbonate. It showed no signs of crystallizing after standing for two months. The free base was thoroughly washed with water and dried over sulphuric acid. A nitrogen determination gave :

	Calculated for $C_{10}H_{14}N_2S$.	Found.
N	14.43	14.78

A nitrogen determination in the hydriodide gave :

	Calculated for $C_{10}H_{14}N_2S.HI$.	Found.
N	8.69	9.03

a-Paratolyl-a-methyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(CH_3)(C_7H_7)N.C(SCH_3)=NCSNHC_6H_5$.—This dithiobiuret resulted by allowing phenyl isothiocyanate to combine with *a*-paratolyl-*a*-methylthiolmethylpseudothiourea at ordinary temperature. The reaction was so energetic that much heat

was evolved. It crystallized from alcohol in elongated prisms and melted at 124°. A nitrogen determination by the Kjeldahl method gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.66

The hydriodide of this base was prepared by saturating a dry benzene solution of the base with hydriodic acid. It separated in the form of minute prisms and melted very sharply with effervescence at 182°. When this salt was mixed with its isomer—the hydriodide of *a*-paratolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret—the mixture gave no definite melting-point, but melted all the way from 162° to 180°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2.HI$.	Found.
N	9.19	9.25

By Morgan S. Elmer.

a,c-Diphenyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHCSNHC_6H_5$.—This was obtained by allowing phenyl isothiocyanate to act on phenylthiolmethylpseudothiourea in ether solution at ordinary temperature. By spontaneous evaporation of the ether a crystalline body was obtained, which crystallized from alcohol in transparent, dog-tooth prisms and melted at 101°. A nitrogen determination gave:

	Calculated for $C_{15}H_{15}N_3S_2$.	Found.
N	13.95	14.45

Thiolmethyl Ester of Phenylthioallophanic Acid, $C_6H_5NHCSNHCOSCH_3$.—This ester was obtained by warming on the steam-bath *a,c*-diphenyl-1-thiolmethylpseudodithiobiuret with 50 per cent hydrochloric acid until complete solution was effected. Mercaptan was slowly evolved during the digestion. Upon cooling the acid solution, a mixture of plates and prisms separated. After several crystallizations from toluene, and then from chloroform, a body was obtained which melted sharply at 157° to 158° with effervescence. It

crystallized from chloroform in plates and a nitrogen determination gave :

	Calculated for $C_9H_{10}ON_2S_2$.	Found.
N	12.40	12.68

a,c-Diphenyl-1,2-thiolmethyldipseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5$.—This base was obtained in the form of its hydriodide by allowing methyl iodide to combine with *a,c*-diphenyl-1-thiolmethylpseudodithiobiuret. The salt crystallized from alcohol in stout prisms and melted with effervescence at 154° to 155°. An iodine determination gave :

	Calculated for $C_{16}H_{18}N_2S_2I$.	Found.
I	2.86	2.73

By treating an alcoholic solution of this hydriodide with a solution of sodium carbonate the free base was immediately precipitated in the form of colorless, needle-like prisms. It was recrystallized from alcohol and melted at 103° to 104°. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.56

a,c-Diphenyl-a-methyl-1-thiolmethylpseudodithiobiuret, $(CH_3)(C_6H_5)N{-}C(SCH_3){=}NCSNHC_6H_5$. — This pseudodithiobiuret resulted when phenyl isothiocyanate was allowed to combine with *a*-phenyl-*a*-methylthiolmethylpseudothiourea in ethereal solution. A colorless solid was formed which crystallized from alcohol in stout prisms and melted at 133° to 134°. A nitrogen determination gave :

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.38

a,c-Diphenyl-1-thiolbenzylpseudodithiobiuret, $C_6H_5N{=}C(SCH_2C_6H_5)NHCSNHC_6H_5$.—This pseudodithiobiuret was obtained by the action of phenyl isothiocyanate on phenylthiolbenzylpseudothiourea. The reaction-product was an oil, which finally solidified after standing about twenty-four hours. It crystallized from alcohol in colorless prisms

and melted at 98° to 100°. It was soluble in benzene and insoluble in water. A nitrogen determination gave :

	Calculated for $C_{21}H_{19}N_3S_2$.	Found.
N	11.14	11.22

Phenylthiolbenzylpseudothiourea and Benzoyl Isothiocyanate.—Among the isothiocyanates which we used in our investigations was included benzoyl isothiocyanate. While the plain aryl isothiocyanates reacted with pseudothioureas generally very slowly with formation of colorless derivatives—dithiobiurets—benzoyl isothiocyanate reacted with such violence that it was necessary to dilute largely with benzene or ether in order to obtain a smooth reaction. It gave strong yellow- or orange-colored derivatives, which were more insoluble in the ordinary solvents than the dithiobiurets, and were insoluble in alkali.

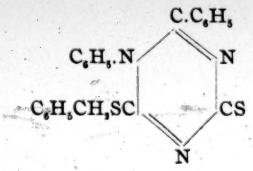
When phenylthiolbenzylpseudothiourea was dissolved in benzene and treated with benzoyl isothiocyanate, so much heat was evolved that it was necessary to connect with a condenser in order to prevent evaporation of the benzene. An oil separated from the benzene which finally solidified to a beautiful, yellow body. It crystallized from benzene in beautiful, yellow, stocky prisms and melted at 190° to 191°. It was insoluble in warm alcohol and water. Nitrogen and sulphur determinations indicated that we were not dealing here with a plain addition-product :

$$C_6H_5N{=}C(SCH_2C_6H_5)NHCSNHCOC_6H_5.$$

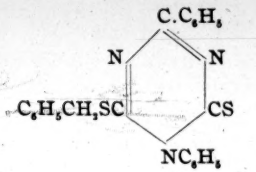
	Calculated for		Found.	
	$C_{22}H_{19}ON_3S_2$.	$(C_{22}H_{17}N_3S_2.)$	I.	II.
N	10.37	10.85	10.88	11.07
S	15.80	16.54	17.24	....

The analytical determinations agreed favorably with the calculated for a triazine derivative. This could result by the loss of a molecule of water from the addition-product of the isothiocyanate and pseudothiourea. Two isomeric triazines are theoretically possible, depending on the point of attack of the isothiocyanate in the pseudourea. Which one of the two

possible forms we are dealing with must be decided by further investigations.



A.



B.

By William B. Cramer.

Orthotolylthiolmethylpseudothiourea, $(o)CH_3C_6H_4N{=}C(SCH_3)NH_2$.—Dixon[1] has recently described this pseudothiourea. We prepared the same by adding methyl iodide to orthotolylthiourea. It agreed in every respect with Dixon's body and melted at 101°. A nitrogen determination gave:

[1] *Loc. cit.*

	Calculated for $C_9H_{12}N_2S$.	Found.
N	15.55	15.95

a-Orthotolyl-c-phenyl-1-thiolmethylpseudodithiobiuret, $(o)CH_3C_6H_4N{=}C(SCH_3)NHCSNHC_6H_5$.—From the action of phenyl isothiocyanate on orthotolylthiolmethylpseudothiourea in ether solution. It separated in beautiful prismatic crystals and crystallized from alcohol in magnificent plates. It was insoluble in water and melted at 114° to 115°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	13.09

a-Orthotolyl-c-phenyl-1,2-thiolmethyldipseudodithiobiuret, $CH_3C_6H_4N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5$.—This base was obtained in the form of its hydriodide by warming on the steam-bath *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret with the calculated quantity of methyl iodide. The hydriodide melted with effervescence at 147° to 148°. The free base was obtained by treating an alcoholic solution of the

salt with sodium hydroxide. It was fairly soluble in alcohol and extremely soluble in benzene. It crystallized from alcohol in stout prisms and melted at 70° to 71°. A nitrogen determination gave :

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.06

a-Phenyl-c-orthotolyl-1-thiolmethylpseudodithiobiuret, $C_6H_5N{=}C(SCH_3)NHCSNHC_6H_4CH_3$.—This biuret was very easily obtained by combining orthotolyl isothiocyanate with phenylthiolmethylpseudothiourea. The reaction was allowed to proceed in ether solution at ordinary temperature. After evaporation of the ether there was obtained a crystalline residue, which crystallized from alcohol in plates and melted at 114° to 115°. When this pseudodithiobiuret was mixed with *a*-orthotolyl-*c*-phenyl-1-thiolmethylpseudodithiobiuret (114° to 115°) the melting-point was lowered to 100° to 103°. A nitrogen determination gave :

	Calculated for $C_{18}H_{17}N_3S_2$.	Found.
N	13.33	13.49

When the above biuret was warmed with a slight excess of methyl iodide an immediate reaction took place with formation of an addition-product. By treating this addition-product with an alcoholic solution of sodium hydroxide a base was immediately precipitated, which crystallized from alcohol in prisms and melted sharply at 70° to 71°. When this was mixed with *a*-orthotolyl-*c*-phenyl-1,2-thiolmethyldipseudodithiobiuret (m. p. 70° to 71°) the melting-point was not altered. A nitrogen determination agreed with the calculated for

$$CH_3C_6H_4N{=}C(SCH_3)NHC(SCH_3){=}NC_6H_5.$$

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.88

a-Orthotolyl-c-phenyl-1-thiolethylpseudodithiobiuret, $CH_3.C_6H_4N{=}C(SC_2H_5)NHCSNHC_6H_5$.—From phenyl isothiocyanate and orthotolylthiolethylpseudothiourea. It crystallized from dilute alcohol in plates and melted at 117° to

118°. It was readily soluble in alcohol, but insoluble in water. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	12.50

When the above dithiobiuret was warmed on the steam-bath with 50 per cent hydrochloric acid, mercaptan was slowly given off. On cooling the acid solution, a mass of plates separated, which crystallized from alcohol in plates or thick tables and melted at 131° to 132°. A nitrogen determination agreed with the calculated for the thiolethyl ester of phenylthioallophanic acid, $C_6H_5NH.CSNHCOSC_2H_5$.

	Calculated for $C_{10}H_{12}ON_2S_2$.	Found.
N	11.66	11.65

a-Phenyl-c-orthotolyl-1-thiolethylpseudodithiobiuret, $C_6H_5N{=}C(SC_2H_5)NHCSNHC_6H_4.CH_3$.—It was necessary to allow phenylthiolethylpseudothiourea and orthotolyl isothiocyanate to stand in ether solution for several days before the reaction was complete. A thick varnish was obtained, which finally was made to crystallize by agitation in a freezing-mixture. It crystallized from alcohol in plates and melted at 95° to 96°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.03

a,c-Diphenyl-1-thiolethylpseudodithiobiuret, $C_6H_5N{=}C(SC_2H_5)NHCSNHC_6H_5$.—From phenyl isothiocyanate and phenylthiolethylpseudothiourea. It crystallized from alcohol in plates and melted at 91° to 93°. A nitrogen determination gave:

	Calculated for $C_{16}H_{17}N_3S_2$.	Found.
N	13.33	12.99

a,c-Diorthotolyl-1-thiolethylpseudodithiobiuret, $CH_3.C_6H_4N{=}C(SC_2H_5)NHCSNHC_6H_4CH_3$. — From orthotolyl isothiocyanate and orthotolylthiolethylpseudothiourea. It crystallized from alcohol in prisms and melted at 86° to 87°. A nitrogen determination gave:

	Calculated for $C_{18}H_{21}N_3S_2$.	Found.
N	12.24	12.41

a,c-Diorthotolyl-1-thiolmethylpseudodithiobiuret, $CH_3.C_6H_4N{=}C(SCH_3)NHCSNHC_6H_4.CH_3$.—From orthotolyl isothiocyanate and orthotolylthiolmethylpseudothiourea. It crystallized from alcohol in plates and melted at 122° to 123°. A nitrogen determination gave:

	Calculated for $C_{17}H_{19}N_3S_2$.	Found.
N	12.76	13.16

NEW HAVEN, CONN.,
May 22, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CIX.—ON SOME MANGANIC PERIODATES.[1]

BY W. B. PRICE.

Although Rammelsberg[2] has asserted that periodate of manganese does not exist, I have found that the following compounds can be easily prepared:

$Na_2Mn_2I_2O_{11}$;

$K_2Mn_2I_2O_{11}$;

and $H_2Mn_2I_2O_{11}$.

These salts form beautiful, bright-red precipitates, which are exactly alike in appearance and are remarkably stable in the absence of reducing agents, since they are apparently entirely insoluble and unchanged when treated with boiling water, boiling dilute or concentrated nitric acid, and boiling dilute sulphuric acid.

The compounds are formed as exceedingly finely-divided precipitates when a solution of manganous sulphate or nitrate containing a large amount of dilute sulphuric or nitric acid is mixed with a sulphuric or nitric acid solution of sodium or potassium periodate, or, in the last case, with periodic acid. The precipitates come down after the lapse of some time in cold solutions, but rapidly upon heating to about 45°. Under

[1] Communicated by H. L. Wells.

[2] Pogg. Ann., 134, 528 (1868).

certain conditions the bright-red precipitates, when in contact with the mother-liquor, become darker in color, evidently from the formation of manganese dioxide. This decomposition is much hastened by heating above 45°, and it apparently depends upon the presence of an excess of manganous salt, which acts as a reducing agent. It is generally best, therefore, when an excess of manganese salt is used, to avoid heating more than necessary, and to separate the precipitate from the liquid by filtration as promptly as possible.

It is evident that Rammelsberg failed to get one of these compounds on account of using nearly neutral instead of strongly acid solutions.

The periodates under consideration, in containing the radical I_3O_{11}, correspond to a number of simple salts of bivalent metals which Rammelsberg prepared and called "quarter-periodates." Taking the sodium salt as an example, the formula, in terms of the oxides, is

$$Na_2O.Mn_2O_3.I_2O_7,$$

or, in terms of two assumed separate salts, it is

$$Na_4I_2O_{11}.Mn_6(I_2O_{11})_3.$$

It is certainly remarkable that compounds which are apparently so basic in their character as these should form in very acid solutions.

In examining these compounds analytically no direct test for periodates could be made, because the substances could not be dissolved without decomposing them. For determining the metals and iodine they were dissolved in sulphur dioxide solution, and the usual gravimetric methods were used. Active oxygen was determined in separate portions by treatment with potassium iodide solution and titration with nearly decinormal sodium thiosulphate. The following analyses were made:

	Calculated for $Na_2Mn_2I_2O_{11}$.	Found. I.	II.	III.
Na	7.85	9.40	7.78	5.82
Mn	18.77	18.41	18.43	16.73
I	43.34	....	42.93	40.90
Active O	24.57	24.55	24.59	22.24

Sample I. was made in the presence of a very large amount of sodium salts and was probably not washed completely free from them; Sample II. was perhaps purer than the others; Sample III. was probably dried only in the desiccator, while the others were dried in a steam-oven. Hence, it seems possible that the salt as formed contains water of crystallization, which is lost at 100°, but this point was not settled.

	Calculated for $K_2Mn_2I_4O_{11}$.	Found. I.	II.	III.
K	12.64	12.04	11.92	8.32
Mn	17.79	17.11	16.89	16.98
I	41.08	41.96	42.41	40.41
Active O	23.29	23.98	24.46	23.37

It should be stated that Analysis III. of both the sodium and potassium compounds, in which the alkali metal found is lower than in the others, was made with products which were probably prepared in the presence of a much greater excess of free acid than in the other cases. It appears possible, therefore, that the alkali metal may be replaced by hydrogen to some extent by the action of a large excess of acid.

The only analytical evidence which has been obtained in regard to the existence of $H_2Mn_2I_4O_{11}$ is the determination of alkalies in a substance, made from a manganous salt and periodic acid, which resembled exactly the sodium and potassium compounds. The amount of alkali-metal sulphates found was only 0.29 per cent.

NEW HAVEN, CONN., May, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CX. — ON RUBIDIUM-BARIUM-SILVER THIOCYANATES.

BY HORACE L. WELLS.

The triple thiocyanates,

$$Cs_2BaAg_2(SCN)_7,$$
$$Cs_2BaCu_2(SCN)_7,$$

and

$$K_2BaAg_2(SCN)_8.H_2O,$$

which were prepared by me last year,[1] show a disagreement

[1] This JOURNAL, 28, 245.

in type between the caesium and potassium compounds. It was of interest, therefore, to know what similar triple compounds would be formed by rubidium, the metal intermediate between caesium and potassium.

As a result of the investigation of this matter, it has been found that a rubidium-barium-silver thiocyanate,

$$Rb_4BaAg_2(SCN)_8.H_2O,$$

exists, which corresponds to the potassium salt, and that another salt,

$$Rb_2BaAg_2(SCN)_6.2(?)H_2O,$$

can be prepared. The latter is not analogous to the caesium salts, but corresponds to a type which was not previously found with barium, but which appears as the most frequently occurring type in the salts,

$$Cs_2CaAg_2(SCN)_6.2H_2O,$$
$$Cs_2MgAg_2(SCN)_6.2H_2O,$$
$$Cs_2MnAg_2(SCN)_6.2H_2O,$$
$$Cs_2NiAg_2(SCN)_6.2H_2O,$$
$$Cs_2NiCu_2(SCN)_6.2H_2O,$$
$$Cs_2CoAg_2(SCN)_6.2H_2O,$$
$$Cs_2CdAg_2(SCN)_6.2H_2O,$$

and $Cs_2CdAg_2(SCN)_6$.

The two rubidium salts under consideration are very soluble, crystallize poorly, and hence are difficult to produce in a satisfactory condition. They were prepared under practically the same conditions, and it is not known what is the cause of the appearance of one instead of the other in a solution.

Attempts to make a rubidium-barium-cuprous thiocyanate were entirely unsuccessful, for appropriate solutions for preparing such a compound evaporated over sulphuric acid to transparent, solid masses without showing signs of crystallization.

4 : 1 : 2, Rubidium-Barium-Silver Thiocyanate, $Rb_4BaAg_2(SCN)_8.H_2O$.—A solution containing rubidium,

barium, and silver thiocyanates in the molecular proportion 3 : 1 : 2 was evaporated over sulphuric acid. When the liquid had become very dense a product was formed which was too unsatisfactorily crystallized to be used for analysis. After a considerable quantity of it had formed, therefore, it was drained as far as possible from the thick mother-liquor by suction on a platinum cone, and then it was dissolved in water and the solution was evaporated over sulphuric acid. This solution did not form good crystals readily, but after repeated trials a crop of large, transparent, prismatic crystals was obtained. These crystals were not well formed and their crystalline form was not determined. No other crop of this salt could be obtained, although several attempts were made to get it; hence the evidence of its existence is confined to the analysis of the single crop, but the correspondence of the composition to that of the potassium salt considerably strengthens the evidence. The results of the analysis are as follows:

	Calculated for $Rb_4BaAg_2(SCN)_8.H_2O$.	Found.
Rb	29.02	....
Ba	11.68	12.36
AgSCN	28.20	28.20
Sol. SCN	29.57	29.30
H_2O	1.53	1.25

2 : 1 : 2, Rubidium-Barium-Silver Thiocyanate, $Rb_2BaAg_2(SCN)_6.2(?)H_2O$.—When attempts were made to prepare other crops of the 4 : 1 : 2 salt under the same and considerably varying conditions, in respect to the mixtures used, and when recrystallizations were made of the first crude crops as in the case described, three fairly satisfactory crops were obtained, but they showed a composition entirely different from the original one. There is doubt about the amount of water in this compound, for the crops, when well pressed upon filter-paper, became very wet when preserved in a corked tube and needed to be dried again before they were analyzed, and when air-dried the substance became somewhat opaque, evidently from loss of water. About 1 molecule of water, or somewhat less, remained in the samples, but since some water had been lost, it is assumed from analogy with other salts of

this type that the original amount of water was probably 2 molecules. The crops were not well crystallized, but they appeared to be homogeneous.

The following analyses were made with air-dry samples. The calculation is made for 1 molecule of water, since this was approximately the amount present:

	Calculated for $Rb_2BaAg_3(SCN)_6.H_2O$.	Found. I.	II.	III.
Rb	19.19	....	....	....
Ba	15.45	13.88	14.61	13.49
AgSCN	37.29	36.07	36.68	37.11
Sol. SCN	26.06	26.06	26.16	25.98
H_2O	2.02	2.32	1.01	1.57

NEW HAVEN, CONN., May, 1903.

THE VOLUMETRIC DETERMINATION OF MERCURY AND OF HYDROCYANIC ACID.

BY LAUNCELOT W. ANDREWS.

It is a familiar fact that hydrocyanic acid is a "pseudo-acid" which possesses no acid reaction at all toward many indicators, as methyl orange, nitrophenol, etc., and which cannot be acidimetrically titrated even with the aid of extremely acid-sensitive indicators, such as phenolphthalein or toluylene-red. If silver nitrate is added to a solution of hydrocyanic acid a quantitative precipitation of silver cyanide occurs, and if the silver salt is in excess, an amount of nitric acid is set free equivalent to the hydrocyanic acid used. Titration of the nitric acid by the aid of any suitable indicator, such as paranitrophenol, leads to a knowledge of the amount of hydrocyanic acid originally present. The process is accurate but not especially convenient. The precipitated silver cyanide may retain free hydrocyanic acid or silver nitrate, or both, according to the conditions of the precipitation, semipermeable "cells" being formed which give up their contents very slowly by long-continued washing, and which continue to exhibit an acid reaction even after washing with excessive amounts of water. This difficulty can be brought within bounds by precipitating from highly dilute solutions. It

might be thought possible to titrate the free nitric acid directly, without filtering from the precipitate, and such is in fact the best mode of proceeding. Nitrophenol is a good indicator for the purpose, although methyl orange may be used. Lacmoid forms an insoluble compound (silver salt?) which disturbs the sharpness of the end-reaction. If the hydrocyanic acid is in excess and silver nitrate from a known amount of metallic silver is employed, an exactly determinate quantity of nitric acid will be set free, and, hence, the titration can be used for the standardizing of acidimetric alkali solutions, the object with which the experiments were originally undertaken. The advantage of using pure metallic silver as the standard is obvious, but the difficulties referred to above, lying in the character of the precipitate, appear here also, in an aggravated form. The attempt to titrate the free nitric acid without filtering from the silver cyanide meets with almost insuperable difficulties when the solution contains an excess of hydrocyanic acid.

In this case, as soon as the free nitric acid is neutralized, the complex salt, potassium argentocyanide, $KAgCy_2$, begins to form in accordance with the reaction

$$HCN + AgCN + KOH = KAg(CN)_2 + H_2O.$$

Potassium argentocyanide is a neutral salt, so that the reaction of the solution changes from acid to neutral as excess of potassium hydroxide is added, instead of from acid to alkaline, and remains neutral until all hydrocyanic acid is converted into potassium argentocyanide. At the same time, the silver nitrate occluded in the precipitate slowly diffuses out, reacting as it does so with the hydrocyanic acid. It is therefore necessary to filter before titrating, and previous to the filtration a digestion for at least twenty-four hours is necessary, during which time the precipitate must be agitated with the solution. It is not thought worth while to give the details of the long series of experiments, since the final result is that the method, while capable of a high degree of accuracy when all precautions are observed, does not possess the simplicity which can be demanded of such a process.

It appeared to the writer to be a question as to how far the completeness of the reaction between hydrocyanic acid and silver nitrate is due to the insolubility of silver cyanide, and how far to its being, possibly, a compound not subject to electrolytic dissociation, that is, not a true salt at all. If the latter were the dominant factor, it should be possible to secure a practically complete reaction between mercuric nitrate or chloride and hydrocyanic acid, since mercuric cyanide is well known to be a non-dissociated compound. If methyl orange is added in small quantity to a solution of pure mercuric chloride and also to a solution of hydrocyanic acid, both solutions remain pure yellow, showing no trace of acid reaction. If the solutions are now mixed together, they turn bright-red. The experiment makes a striking lecture experiment illustrative of the theory of electrolytic dissociation. Nitrophenol, lacmoid paper, or even a rather insensitive, strongly blue, litmus paper can be used instead of methyl orange to show the liberation of hydrochloric acid, *i. e.*, the production of hydrogen ions. The reaction,

$$HgCl_2 + 2HCN = Hg(CN)_2 + 2HCl,$$

is not instantaneous, but is practically complete, and the disturbing factors mentioned above as occurring in the reaction between silver salts and hydrocyanic acid, are absent. It appears, therefore, probable that silver cyanide also is a non-dissociated compound, and that the so-called "elective affinity" between cyanogen and silver is a phenomenon due to this fact rather than to the low solubility of silver cyanide, a supposition with which the known fact that an alkali cyanide reacts quantitatively with silver chloride to form silver cyanide is in the best of harmony.

The possibility of the application of these relationships to the acidimetric titration of mercury or of hydrocyanic acid and the cyanides lies very near. In the sequel it is shown that the possibility can easily be realized. It may be said that no new method for the titration of hydrocyanic acid is needed, since that of Liebig,[1] as modified by Denigés,[2] answers

[1] Ann. Chem. (Liebig), 77, 102 (1851).
[2] Ann. chim. phys. [7], 6, 381 (1895).

all practical requirements. It is to be noted, however, that the application of Liebig's method requires a perfectly clear solution, whereas pharmaceutical preparations of hydrocyanic acid are frequently turbid. The addition of a new and convenient method of titration to the small number of those already known for the determination of mercury cannot be regarded as a work of supererogation, especially when the new method, as is the case with that described, is applicable to the determination of mercuric chloride in the highly dilute solutions of that substance employed by surgeons.

Determination of Hydrocyanic Acid and Cyanides.

For this determination the following solutions are required: *a*, decinormal solutions of hydrochloric acid and of potassium (or sodium) hydroxide; *b*, a nearly saturated solution of mercuric chloride, containing about 40 grams of the pure recrystallized salt per liter. The exact strength of this solution need not be known; *c*, a saturated solution of pure paranitrophenol in water. This is to be preferred to the solution in alcohol often recommended as an indicator. The aqueous solution keeps indefinitely in the light or in the dark.

To determine hydrocyanic acid or a simple cyanide, dilute the solution till it contains not more than about 1 per cent of hydrocyanic acid and add 2 drops of nitrophenol solution. If this imparts a yellow color, add decinormal hydrochloric acid until the color has all but disappeared; if it is colorless, add decinormal potassium hydroxide till the solution shows a very pale yellow. Now, add an excess of the mercuric chloride solution (usually 15 or 20 cc.), stir and allow to stand for one hour at the temperature of the air.

A solution of hydrocyanic acid which had by gravimetric analysis been found to contain 3.40 per cent, was analyzed by the above method. For that purpose, 50 cc. was measured by a pipette into a 500 cc. flask, filled to the mark, and shaken. Five cc. of this solution were mixed with 10 cc. of an approximately decinormal mercuric chloride solution, allowed to stand for an hour, and then titrated as described. Re-

quired, 6.30 cc. of N/10 KOH, equivalent to 0.01704 gram of hydrocyanic acid, or 3.408 per cent found.

Twenty cc. of the same solution were mixed with 10 cc. of an approximately 4 per cent mercuric chloride solution and the liquid allowed to stand three hours. Required, 25.03 cc. of decinormal potassium hydroxide, equivalent to 0.0677 gram of hydrocyanic acid or 3.385 per cent (on original solution) found.

From the original solution was prepared, by suitable dilution, a semi-normal hydrocyanic acid solution, containing, by calculation, 13.52 grams per liter. Five cc. of this solution were mixed with 33 cc. of the last-mentioned mercuric chloride solution, and, after standing fifteen minutes, were titrated in the usual way. Required, 24.78 cc. of decinormal potassium hydroxide, equivalent to 0.06703 gram of hydrocyanic acid or 1.34 per cent found. The small deficit observed here is probably due to a slight volatilization of hydrocyanic acid during the manipulations incidental to dilution and exposure.

Determination of Mercury.

The only solution required, in addition to those mentioned above, is an approximately normal solution of hydrocyanic acid neutral to nitrophenol. Such a solution may be conveniently prepared in the following way without distillation: Dissolve 68 to 80 grams of the best commercial potassium cyanide in 0.5 liter of water, add about 5 grams of barium chloride in saturated solution, and filter, thus removing carbonates which would interfere with the exact neutralization. To the filtrate add about 10 cc. of the nitrophenol solution (*vide supra*), and then dilute sulphuric acid till the yellow color has become pale, finishing the neutralization with decinormal hydrochloric acid. Finally, make up to a liter, disregarding the barium sulphate which may be allowed to subside. This solution should contain about 27 grams of hydrocyanic acid and be colorless.

The mercury to be determined must be present as mercuric chloride (or bromide?). If in the form of nitrate, a small excess of sodium chloride is added. Organic acids must be ab-

sent. It is next to be made neutral by addition of nitrophenol, avoiding undue excess, and hydrochloric acid till the yellow color is just on the point of disappearing. To the solution so prepared an excess of the neutral hydrocyanic acid solution is added and the mixture set aside for not less than one hour for the completion of the reaction. The hydrochloric acid formed is titrated with potassium hydroxide, decinormal or centinormal, according to the dilution of the mercuric solution, until a permanent pale-yellow tint is visible. A very small excess of hydrocyanic acid suffices, and an unnecessary excess is for obvious reasons to be avoided. To be sure that sufficient hydrocyanic acid is present, if in doubt, add a few drops at the conclusion of the titration. This will instantly destroy the yellow color if insufficient had been present, but otherwise will not affect it. The method has been repeatedly used by students in this laboratory with very satisfactory results, in part for the determination of mercuric chloride in solutions containing one part in ten thousand. They have with it obtained much better results than by the method of Vitali[1] for the examinatlon of dilute solutions, and in considerably less time. Vitali's method consists in boiling the mercuric chloride solution with an excess of sulphurous acid, expelling the excess, and titrating acidimetrically the sulphuric and hydrochloric acids formed. The method is satisfactory for stronger solutions of mercuric chloride, but certain sources of error which are inappreciable in concentrated solution become serious when the solution is highly dilute. These are oxidation of the sulphurous acid by the atmosphere, imperfect expulsion of the last traces of sulphurous acid, reduction of the mercury too far, *i. e.*, to metal. Prolonged boiling is needed to drive off the last of the sulphur dioxide, which passes off rapidly at first, but with extreme slowness when only a little is left. Reduction of the mercurous chloride to metal is hindered by the considerable amount of hydrochloric acid present in more concentrated solutions, but in those of high dilution the amount of acid is insufficient to have this effect. The precipitate in the latter

[1] Bolletino Chimico Farmaceutico, 1894, 365.

case often becomes gray. All these sources of error lead to the results of the determination being too high.

That the cyanide method also gives correct results with more concentrated solutions is shown by the following test analyses:

A solution was prepared containing 6.780 grams of pure mercuric chloride in 500 cc. It was perfectly neutral to nitrophenol. To 5 cc. of it, 2 cc. of a hydrocyanic acid solution (3.4 per cent) was added, and 1 drop of nitrophenol solution. Required, 5 cc. of decinormal potassium hydroxide, equivalent to 0.0678 gram found. Twenty-five cc. of the same solution, with 5 cc. of hydrocyanic acid, required 25 cc. of the standard alkali, equivalent to 0.339 gram of mercuric chloride found. Again, 25 cc. of the same solution, with 10 cc. of hydrocyanic acid and 100 cc. of water, required 25.03 cc. of the hydroxide, equivalent to 0.3394 gram of mercuric chloride found.

Since mercuric chloride is a substance which can be easily obtained in a high state of purity and is in every way well defined, it is suited as a standard for acidimetric solutions, the sharpness of the method of titration which has been described making it readily available for this purpose.

The results quoted of themselves show the practicability of this method, of which I shall have something more to say in connection with a discussion of other methods of standardization.

CHEMICAL LABORATORY,
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May 16, 1903.

THE ASSOCIATION OF A LIQUID DIMINISHED BY THE PRESENCE OF ANOTHER ASSOCIATED LIQUID.

BY HARRY C. JONES AND GRANTLAND MURRAY.

Ramsay and Shields,[1] in their beautiful investigation on the surface-tension of liquids, showed conclusively that the molecules of certain liquids are made up of a number of the simplest molecules, while the molecules of other liquids are iden-

[1] Ztschr. phys. Chem., 12, 433 (1893).

tical with the simple chemical molecule. They pointed out that if we represent the degree of association, or the association factor, by x, that

$$x\frac{2}{3} = \frac{2.12}{k},$$

in which k, the differential coefficient for the liquid between any two known temperatures, can be calculated by measuring the surface-tension of the liquid at the temperatures in question, knowing the molecular volume at these temperatures.

If the liquid is not associated the value of this coefficient is 2.12. If the liquid is associated the value of the coefficient k is always less than 2.12, and the association factor, x, or number of molecules associated to form the molecule of the liquid, can be calculated thus:

$$x = \left(\frac{2.12}{k}\right)^{\frac{3}{2}}.$$

Ramsay and Shields showed that of the common liquids water has the highest association factor, its molecule at 0° being made up of 4 molecules of the composition H_2O, or has the composition $(H_2O)_4$. The alcohols of the methyl alcohol series are also strongly associated liquids, especially the first members of the series, and the same holds for the formic acid series of acids; formic and acetic acids being especially strongly aggregated compounds.

The above investigation acquired a new interest when Dutoit and Aston[1] pointed out that there is a connection between the association of any solvent and its own dissociating power. It was made probable that only those liquids whose molecules are polymerized or associated have the power of breaking down or dissociating the molecules of electrolytes into ions. This relation is obvious in the case of water, which is the most highly associated liquid, and which, of all the common solvents, has the greatest ionizing power.

The present investigation was undertaken with the object of determining the effect of one associated liquid on the association of another associated liquid. This line of work was

[1] Compt. rend., **125**, 240 (1897).

suggested by an investigation[1] which was carried on in this laboratory last year. The investigation in question had to do with the relation between the conductivity of salts in water, methyl, ethyl, and propyl alcohols, and in mixtures of these solvents. It was found that the conductivity of the salt in the mixed solvents was very frequently less, for a given concentration, than in the lower conducting of the two solvents present in the mixture. This was established in mixtures of methyl alcohol and water for a number of salts, such as potassium iodide, ammonium bromide, strontium iodide, and lithium nitrate, the salt conducting less in the mixture of methyl alcohol and water than in pure methyl alcohol. Ethyl alcohol and water at 0° showed a similar phenomenon for all the salts investigated.

Salts dissolved in a mixture of equal parts of methyl and ethyl alcohols do not conduct less than in pure ethyl alcohol, but show a conductivity which is less than the mean of the conductivities of the substances in the pure solvents at the same dilution. This is obviously a result of the same general character as that obtained with mixtures of the alcohols and water. This investigation was extended to a number of mixtures of the different solvents at different temperatures, and the concentrations of the solutions of salts which were employed were varied greatly. The results were of the character indicated.

At first sight it was extremely difficult, not to say impossible, to interpret these results. How could an electrolyte in a mixture of methyl alcohol and water be dissociated less than in pure methyl alcohol, when water had a much higher dissociating power than methyl alcohol? This could be explained most easily on the assumption that each solvent so acted on the other as to diminish its dissociating power, and this suggestion[2] was made as a possible explanation of the results.

At the time the suggestion was made the evidence bearing upon the case was very meagre indeed. It was known that methyl and ethyl alcohols, whose molecules in the pure,

[1] Jones and Lindsay: This JOURNAL, **28**, 329 (1902).
[2] Lindsay: *Ibid.*, **28**, 369 (1902).

homogeneous liquids are considerably aggregated, give normal molecular weights when dissolved in water.[1] This evidence, however, was far from sufficient to justify any general conclusion on the subject. In order to determine whether associated liquids have any general influence on each other's association, it is necessary to take associated liquids and determine the molecular weights of each in the other, and then compare the results with the molecular weights of the several liquids in the pure condition.

There are not many liquids which can be employed in this work, since the boiling-point method of determining molecular weights cannot be used for any liquid dissolved in another liquid. We are, therefore, limited to the freezing-point method, and of those liquids whose association is known, only a few freeze at temperatures to which the freezing-point method can be applied.

Liquids Used in this Work.

We have found three liquids which fulfil in an admirable manner the conditions necessary for this work, *i. e.*, they must dissolve readily in one another, must not act chemically upon one another, must not undergo appreciable electrolytic dissociation, and must be strongly associated substances. These liquids are water, acetic acid, and formic acid.

Purification of the Liquids.

The water used in this investigation was purified by double distillation. It was first distilled from chromic acid, which destroyed the organic matter and retained the ammonia, and then from barium hydroxide, which retained the carbon dioxide. Its conductivity was 1.2×10^{-6}.

The acetic acid was furnished by Bender and Hobein for cryoscopic work. This was fractionally crystallized, using a large volume at the outset and discarding about half at each crystallization. After the freezing-point showed that the material was nearly pure, a relatively smaller amount was discarded at each crystallization. After ten crystallizations a

[1] Jones: Ztschr. phys. Chem., 12, 623 (1893).

specimen was obtained which froze sharply at 16°.5, and which was, therefore, practically pure acetic acid.

It was found to be much more difficult to obtain formic acid free from water. The purest specimen that could be purchased was treated with a large amount of phosphorus pentoxide and distilled. The formic acid was decomposed to some extent by the pentoxide into carbon monoxide and water, but the amount of water removed in this way was very much greater than the amount formed as the result of the decomposition of the acid. The product resulting from the distillation was then subjected to fractional crystallization. After freezing out the acid fifteen or twenty times, discarding in each case a considerable volume, a product was obtained which froze at 7°. *The statement in the literature that formic acid freezes below zero and melts at 8°.5 is, therefore, erroneous.* The specimen which fulfilled these conditions must have contained considerable water. Such a specimen would freeze only when cooled considerably below its melting-point, and the crystals which separated, being comparatively free from water, would then melt close to the true melting-point of the acid.

With the above liquids the following measurements were made by the freezing-point method :

I. The molecular weight of water in acetic acid.
II. The molecular weight of water in formic acid.
III. The molecular weight of acetic acid in water.
IV. The molecular weight of acetic acid in formic acid.
V. The molecular weight of formic acid in water.
VI. The molecular weight of formic acid in acetic acid.

Results.

The results are given in the following tables. Column I. contains the amount of solvent used ; Column II. the amount of liquid whose molecular weight was to be determined ; Column III. the concentration in terms of normal, a normal solution being defined as one that contains a gram-molecular weight of the electrolyte in 1,000 grams of the solvent ; Column IV. gives the freezing-point lowerings actually observed ;

and Column V. the molecular weight of the liquid at the concentration in question. In all of this work care was taken to keep the temperature of the freezing-mixture only a little below the freezing-point of the solution.

Water (18) in Acetic Acid.

I. Acetic acid.	II. Water.	III. Concentration.	IV. Lowering.	V. Molecular weight.
39.68	0.454	0.64	2°.06	21.7
38.32	0.514	0.75	2°.38	22.0
"	0.820	1.19	3°.58	23.3
39.68	0.947	1.33	3°.93	23.7
"	1.547	2.17	5°.89	25.8
"	2.061	2.89	7°.45	27.2
"	2.541	3.56	8°.79	28.4
38.32	2.637	3.82	9°.33	28.8
39.68	2.992	4.19	9°.95	29.6
"	3.870	5.42	12°.11	31.4
"	4.686	6.56	14°.00	32.9
"	5.589	7.83	16°.04	34.2
"	6.472	9.06	17°.86	35.6
"	7.566	10.59	20°.07	37.1
"	8.559	11.98	22°.00	38.2
"	9.032	12.65	22°.90	38.8

Water (18) in Formic Acid.

I. Formic acid.	II. Water.	III. Concentration.	IV. Lowering.	V. Molecular weight.
48.24	0.808	0.93	2°.35	19.7
"	1.325	1.53	3°.75	20.3
"	2.204	2.54	6°.13	20.6
"	3.060	3.52	8°.30	21.2
"	4.434	5.13	11°.69	21.8
"	5.376	6.18	14°.11	21.9

Acetic Acid (60) in Water.

I. Water.	II. Acetic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
37.15	0.376	0.17	0°.34	55.4
"	3.959	1.78	3°.30	60.1
"	6.830	3.06	5°.45	62.7
50.65	10.794	3.56	6°.19	64.0
62.17	17.474	4.70	7°.85	66.6
37.15	10.771	4.83	8°.05	67.0
37.15	15.728	7.06	10°.92	72.1

Acetic Acid (60) in Formic Acid.

I. Formic acid.	II. Acetic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
40.35	0.433	0.18	0°.48	61.9
34.23	1.018	0.50	1°.27	64.9
40.35	1.593	0.66	1°.65	66.3
34.72	1.835	0.88	2°.16	67.8
34.23	2.256	1.10	2°.67	68.4
38.49	2.873	1.24	2°.98	69.4
34.72	3.968	1.90	4°.45	71.1
38.49	6.464	2.80	6°.29	74.0
34.72	10.708	5.14	10°.97	77.9
34.23	10.764	5.24	11°.16	78.0
"	18.838	9.17	18°.19	83.8

Formic Acid (46) in Water.

I. Water.	II. Formic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
35.10	0.546	0.34	0°.64	45.2
193.67	7.850	0.88	1°.62	46.5
35.10	1.667	1.03	1°.89	46.7
"	4.928	3.05	5°.28	49.5
136.79	31.564	5.03	8°.50	50.5
141.43	40.109	6.16	10°.34	51.0

Formic Acid (46) in Acetic Acid.

I. Acetic acid.	II. Formic acid.	III. Concentration.	IV. Lowering.	V. Molecular weight.
30.41	1.152	0.82	2°.93	50.4
"	1.702	1.22	4°.26	51.2
"	2.303	1.65	5°.66	52.2
"	2.820	2.02	6°.84	52.9
"	3.410	2.44	8°.10	54.0
"	4.267	3.05	9°.93	55.1
"	5.098	3.64	11°.55	56.6
"	6.136	4.39	13°.53	58.2
"	7.024	5.02	15°.24	59.1
50.64	14.814	6.36	18°.40	62.0
30.02	11.403	8.26	22°.54	65.7

These results are plotted in curves. The molecular weight of water in acetic acid and formic acid with varying concen-

tration in Fig. I., the molecular weight of acetic acid in water and in formic acid in Fig. II., and the molecular weight of formic acid in water and in acetic acid in Fig. III.

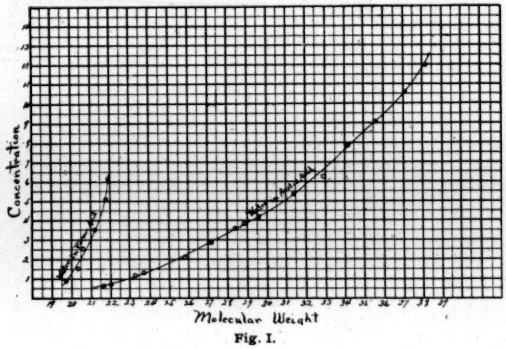


Fig. I.

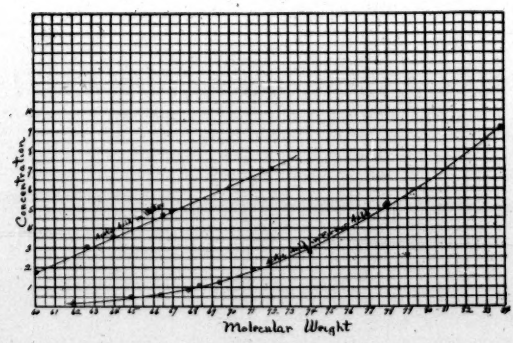


Fig. II.

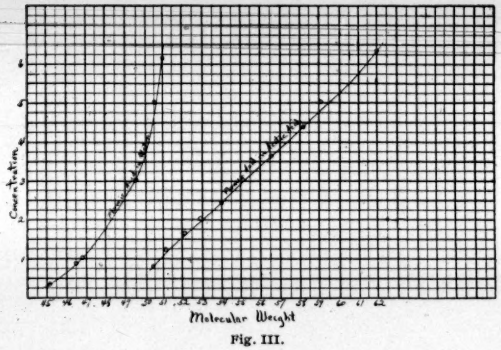


Fig. III.

Discussion of Results.

The molecular weight of water in acetic acid at the greatest dilution used (0.64 normal) is 21.7, which is only slightly greater than the molecular weight corresponding to the composition H_2O. In the most concentrated solution used, which is somewhat more than twelve times normal, the molecular weight of the water is a little more than would correspond to the composition $(H_2O)_2$. In pure water, however, we know, from the work of Ramsay and Shields, that the molecules have the composition $(H_2O)_4$. The association of water is, therefore, greatly diminished by the presence of the associated solvent, acetic acid.

The same remarks apply to solutions of water in formic acid. At the greatest dilution, the molecular weight of the water is only slightly above normal, the molecular weight increasing slightly as the concentration of the solution increases. The complex molecules of water are broken down to even a greater extent by formic acid than by acetic acid. This is in keeping with the relative powers of these two solvents to break molecules down into ions, formic acid being a much stronger dissociant than acetic acid.

The molecular weight of acetic acid in water is approxi-

mately normal for the more dilute solutions investigated, increasing somewhat above normal in the more concentrated solutions. The amount of electrolytic dissociation of even the most dilute solutions of acetic acid in water is so small as to exercise only a slight influence on the results.

Pure acetic acid, at the freezing temperature, is a very much associated liquid. The work of Ramsay and Shields[1] has shown that the differential coefficient k for acetic acid between 16° and 46°, is 0.9. The association

$$x = \left(\frac{2.12}{0.9}\right)^{\frac{1}{2}} = 3.6.$$

It is, therefore, obvious that the association of acetic acid is greatly diminished by water.

The molecular weight of acetic acid in formic acid is greater than in water at the same concentrations, ranging from 61.9 to 83.8 for the different concentrations employed. This, again, is what we might expect. Water having a greater power than formic acid to break molecules down into ions, also has a greater power to break down complex molecules into simpler ones. In no case, however, is the molecular weight of acetic acid in formic acid greater than about one and one-fourth the simplest molecular weight, showing that the complex molecules of pure acetic acid are greatly decomposed by the formic acid.

The same remarks apply, in general, for formic acid in water and in acetic acid. Formic acid, in the pure condition, is associated to just about the same extent as acetic acid. Ramsay and Shields[2] found the coefficient k for formic acid to be 0.902. Therefore, the association is,

$$x = \left(\frac{2.12}{0.902}\right)^{\frac{1}{2}} = 3.6.$$

The molecular weight of formic acid in water is only slightly greater than normal, even at the greatest concentration employed. In acetic acid the molecular weight is greater than in water at the same concentration. This is

[1] Ztschr. phys. Chem., 12, 469 (1893).
[2] *Ibid.*, 12, 469 (1903).

analogous to what has been found with the other solvents employed. Water has the greater power to break down molecules into ions, and also the greater power to decompose molecular complexes into simpler molecules.

Effect of the Dissolved Substance on the Constant of the Solvent.

The above results show that the associated molecules of the dissolved substance are broken down by the solvent into simpler molecules. It is also true that the molecules of the solvent are broken down into simpler molecules by the molecules of the dissolved substance. The magnitude of this influence will depend upon the concentration of the solution and the state of aggregation of the dissolved substance in the solution. It is not a simple matter to determine the exact magnitude of the effect on the solvent, which will be produced in any given case.

In the calculation of the molecular weights of the dissolved substances, given above, the freezing-point constant of the solvent is assumed to be constant. Since the dissolved liquid diminishes the association of the solvent, it will, from Raoult's law, diminish the freezing-point constant of the solvent. This effect will become appreciable only when the concentration of the solution has become considerable. As the freezing-point constant becomes less the molecular weight as calculated from the observed freezing-point lowering would be less than that given above. The effect of this influence of the dissolved substance on the solvent would, then, be to give still smaller molecular weights for the former than those calculated above, especially for the more concentrated solutions. In a word, to show a still greater diminishing of the association of the dissolved substance by the solvent than would be indicated by the above results. This would change somewhat the position of the curves, especially in the more concentrated solutions, but in such a way as to augment the effect, which is shown so clearly by them.

Further, in the more concentrated solutions it is not at all certain that the pure solid phase of the solvent separated from the solution. This may have been mixed with the solid

phase of the liquid present in the smaller quantity. The result would have been to give a smaller lowering of the freezing-point, and, consequently, a higher molecular weight for the dissolved substance.

Since both of the above effects manifest themselves to an appreciable extent only in the more concentrated solutions, the results, as found experimentally in the more dilute solutions, may be regarded as very close to the true molecular weights of the several liquids when dissolved in one another. In the more concentrated solutions the true molecular weights are smaller than those found by experiment. The latter show a very marked diminution in the complexity of the molecule in solution, as compared with the pure state. This would be still more obvious if the exact molecular weight of the dissolved liquid in concentrated solutions could be determined.

Explanation of the Results Obtained by Jones and Lindsay.

In the light of the above facts the results obtained by Jones and Lindsay are easily explained. An electrolyte conducts less in a mixture of methyl alcohol and water because these two strongly associated solvents diminish each other's association, and, since each diminishes the association of the other, it diminishes the dissociating power of the other solvent. The dissociation of an electrolyte in the mixed solvents is less than in the lower dissociating solvent, and, consequently, the conductivity is less in the mixed solvents.

The position of the minimum in the curve expressing the relation between molecular conductivity and concentration of alcohol in the mixed solvents can be also readily interpreted, now that we know the effect of one associated solvent on the association of another associated solvent.

The minimum conductivity shown by a solution of an electrolyte of given concentration, in mixtures of water and alcohol, corresponds to that particular mixture of alcohol and water which has the least dissociating power. This is the same as to say, to that particular mixture of alcohol and water in which, at the temperature in question, the association of each solvent is at a minimum. This mixture, at

which the minimum conductivity occurs, is the particular mixture of the two solvents in which each has diminished the association of the other to a maximum extent.

It is worthy of note that the position of the minimum changes with change in temperature, occurring at the more elevated temperature in the mixture of alcohol and water containing more alcohol. This may have to do with the fact that the critical temperature, or the temperature at which all association disappears, is less for methyl, ethyl, and propyl alcohols than for pure water. Therefore, the effect of a given rise in temperature would probably be to decrease the association of the alcohols more than that of water. This influence would add itself to that resulting from the effect of each of the solvents on the association of the other, and would show the minimum dissociation, and, consequently, the minimum conductivity in the region where there was more alcohol and less water present. This seems to us to be a possible explanation of the otherwise unexplained fact that the minimum in the conductivity curve is shifted with change in temperature.

We propose to extend this investigation, especially to the action of non-associated solvents on the association of associated solvents.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
April, 1903.

THE LOWERING OF THE FREEZING-POINT OF AQUEOUS HYDROGEN DIOXIDE BY SULPHURIC AND ACETIC ACIDS.

BY HARRY C. JONES AND GRANTLAND MURRAY.

The lowering of the freezing-point of aqueous hydrogen dioxide, produced by certain salts, was first measured in this laboratory about two years ago.[1] The salts that were studied were potassium chloride, sodium nitrate, and potassium nitrate. The lowering of the freezing-point of aqueous hydrogen dioxide was compared with the lowering of the freezing-point of water produced by these same substances, with the

[1] Jones, Barnes, and Hyde: This JOURNAL, 27, 22 (1902).

result that they were found to lower the freezing-point of water to a greater extent than the freezing-point of the dioxide.

The work begun by Jones, Barnes, and Hyde was extended by Jones and Carroll[1] to ammonium sulphate and also to sulphuric and oxalic acids. Results were obtained with ammonium sulphate which were of the same general character as those yielded by the salts earlier investigated. Ammonium sulphate lowered the freezing-point of water to a greater extent than the freezing-point of hydrogen dioxide.

The results with sulphuric and oxalic acids were quite different from those obtained with salts. The acids produced a greater lowering of the freezing-point of the dioxide than of water. Only a few measurements, however, were made with the acids, and the object of the present investigation was to repeat and extend the earlier work in this field.

We have worked with sulphuric acid, which is strongly dissociated, and with acetic acid which is only slightly dissociated. The hydrogen dioxide was purified exactly as in the earlier work. The sulphuric acid was added slowly to the aqueous solution of the dioxide, which was kept surrounded by ice to prevent the temperature from rising appreciably. The concentration of not only the original hydrogen dioxide was ascertained, but also the concentration of the dioxide after the sulphuric acid had been added, and the freezing-point of the solution determined. The strength of the aqueous solution of hydrogen dioxide was always ascertained by titrating against a standard solution of potassium permanganate.

The Results with Sulphuric Acid.

The sulphuric acid which was employed was only 96 per cent H_2SO_4. The corresponding correction for the 4 per cent of water was introduced.

The change in the concentration of the solution, due to the separation of ice from the undercooled liquid, was corrected, taking into account the effect of the presence of both hydrogen dioxide and sulphuric acid.

[1] This JOURNAL, 28, 284 (1902).

In the following tables, Column I. gives the percentage concentration of the hydrogen dioxide; Column II. the concentration of the sulphuric acid in terms of gram-molecules per liter; Column III. the corrected lowering of the freezing-point; and Column IV. the molecular lowering of the freezing-point.

The results[1] with sulphuric acid and water are:

II.	III.	IV.
1.0	4°.190	4°.190
0.5	2°.030	4°.060
0.3	1°.173	3°.910
0.1	0°.396	3°.960

The following results were obtained with sulphuric acid in aqueous hydrogen dioxide:

I.	II.	III.	IV.
4.64	1.209	6°.263	5°.18
4.74	0.710	3°.311	4°.66
4.77	0.511	2°.293	4°.49
4.84	0.337	1°.490	4°.41
9.34	0.771	4°.263	5°.53
8.84	0.680	3°.757	5°.52
9.00	0.519	2°.838	5°.47
9.53	0.484	2°.526	5°.22
10.19	0.470	2°.432	5°.14
8.83	0.328	1°.630	4°.97
9.15	0.242	1°.165	4°.81
9.73	0.138	0°.717	5°.19

These results are of the same general character as those obtained by Jones and Carroll. The freezing-point of hydrogen dioxide is lowered to a much greater extent by sulphuric acid than the freezing-point of water, and just as we would expect, the molecular lowering is greater the more concentrated the solution of hydrogen dioxide.

The Results with Acetic Acid.

The acetic acid was prepared by fractionally crystallizing the purest specimen which could be obtained commercially, until the melting-point showed that practically all the water had been removed. The same precautions and corrections

[1] Jones and Carroll: This JOURNAL, 28, 291 (1902).

were introduced with the acetic acid as with sulphuric acid. The change in the concentration of the hydrogen dioxide, produced by the addition of the acetic acid, and the change in concentration due to undercooling, were taken into account and the corresponding corrections applied. The lowering of the freezing-point of water by acetic acid was determined, and the following results obtained :

II.	III.	IV.
4.251	8°.80	2°.07
2.715	5°.40	1°.99
2.121	4°.176	1°.97
1.358	2°.592	1°.91
1.063	2°.020	1°.90
0.530	1°.000	1°.89
0.266	0°.507	1°.91
0.133	0°.276	2°.08
0.0665	0°.140	2°.11

The lowering of the freezing-point of water produced by acetic acid is about what we would expect from its small dissociation, and the minimum in the molecular lowering, calculated on the above basis, is analogous to what was found by Jones and Getman[1] for such a large number of electrolytes.

The following results were obtained with acetic acid in aqueous hydrogen dioxide of varying concentration. Two series of measurements were made, in which the strengths of both the hydrogen dioxide and the acetic acid were varied. The results are given below :

I.	II.	III.	IV.
3.57	4.186	8°.869	2°.12
3.75	2.093	4°.241	2°.02
3.90	1.272	2°.520	1°.99
4.03	0.567	1°.058	1°.87
7.88	1.902	4°.137	2°.17
8.05	1.122	2°.301	2°.05
8.22	0.454	0°.900	1°.98
7.89	0.136	0°.257	1°.88

A comparison of the lowerings in water and in aqueous hydrogen dioxide will show that the latter are somewhat

[1] This JOURNAL, 27, 433 (1902).

greater than the former, and are, therefore, analogous to the results obtained with sulphuric acid.

While the lowering of the freezing-point of aqueous hydrogen dioxide produced by salts and bases is less than the lowering of the freezing-point of water produced by the same concentrations of the same substances, the lowering of the freezing-point of aqueous hydrogen dioxide produced by acids is greater than the lowering of the freezing-point of water produced by these same substances. The explanation of the results obtained with salts and bases, already suggested,[1] seems to be quite satisfactory. These compounds in solution unite with the hydrogen dioxide, forming complex, unstable substances. This conclusion, as has already been pointed out, is in accord with the recent work of Tanatar.[2]

The acids seem to be more strongly dissociated by hydrogen dioxide than by water, and, consequently, produce a greater lowering of the freezing-point of the former solvent. This conclusion is in accord with the work of Calvert,[3] who showed that the dielectric constant of hydrogen dioxide is probably higher than that of water.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
June, 1903.

THE ACTION OF ACETYL CHLORIDE ON SELENIC ACID.

BY ARTHUR B. LAMB.

Several attempts have been made to secure selenium trioxide, *i. e.*, the anhydride of selenic acid. None of them have been distinctly successful, though for a number of reasons one would suppose that such a body might exist. The analogous oxide of sulphur, for instance, is decidedly stable. Again, the stability of selenium dioxide, considered in connection with the very generally increasing stability of acidic oxides with their increasing oxygen content, points in the same direction.[4]

[1] This JOURNAL, **28**, 290 (1902).
[2] Ztschr. anorg. Chem., **28**, 255.
[3] Ann. d. Phys., **1**, 483.
[4] Michael and Conn: This JOURNAL, **23**, 444.

Cameron and Maccallan[1] seem to have most nearly succeeded in securing this body. They digested selenic acid, which they for the first time had been able to obtain anhydrous, with phosphoric anhydride. A white, granular precipitate resulted, which some unpublished analyses roughly indicated to be selenium trioxide.

A repetition of this experiment by the writer gave a similar precipitate, but in too small amounts for a quantitative analysis. Qualitative tests, however, showed a partial reduction to selenious acid, which might indicate a partial dehydration, and subsequent evolution of oxygen.

Digestion of the acid with anhydrous perchloric acid was also tried. The perchloric acid was prepared according to the method given by Michael and Conn.[2] Both an anhydrous selenic acid and an acid containing a slight amount of water were employed. The digestions were continued from three to four hours at 100° and 140°. At the end, however, in every case the perchloric acid could be distilled off unchanged.

The action of pure, dry acetyl chloride was then tried, and, while the anhydride of selenic acid was not obtained, a reaction of some interest was brought to light.

The selenic acid used in this, as well as in the previous experiments, was prepared in successive steps from pure selenium according to methods described by Thomsen,[3] and by Cameron and Maccallan. The resulting acid melted at 57°. The true melting-point of the acid as given by Cameron and Maccallan is 58°, and as very slight amounts of water greatly lower the melting-point, the acid as prepared was evidently nearly anhydrous. It contained, however, a trace of selenious acid, as shown by the faint coloration of its aqueous solution on the passage through it of hydrogen sulphide gas.

To the selenic acid, immersed in a bath of ice-water, the acetyl chloride, cooled to 0°, was added. A very energetic reaction ensued, with the immediate precipitation of a white, granular substance and the evolution of much gas. The white precipitate at first redissolved, but on the addition of

[1] Proc. Roy. Soc. (London), **46**, 13; Chem. News, **59**, 269.
[2] This JOURNAL, **23**, 444.
[3] Ber. d. chem. Ges., **2**, 598.

more acetyl chloride became permanent and copious. It was found to be very hygroscopic, fuming strongly of hydrochloric acid when exposed to the air, and rapidly liquefying. Indeed the sulphuric acid in a desiccator must be very strong, else the substance will deliquesce even there. Qualitative tests by means of barium chloride and hydrochloric acid showed the complete reduction of the selenic acid to the selenious condition. Chlorine was also shown to be present in considerable amount.

Samples of the precipitate were prepared for analysis by drying in a vacuum over strong sulphuric acid. The selenium was determined by the precipitation of the free element with sulphur dioxide and weighing on tared filters. The chlorine was determined as silver chloride.

I. 0.1872 gram substance gave 0.0743 gram Se.
II. 0.2431 gram substance gave 0.0921 gram Se.
III. 0.2021 gram substance gave 0.5116 gram AgCl.
IV. 0.1702 gram substance gave 0.4247 gram AgCl.

	Calculated for $SeCl_4$.	Found. I.	II.	III.	IV.
Se	35.81	39.7	37.9	...	...
Cl	64.19	...	...	62.6	61.7

The physical properties, qualitative tests, and the analytical results, all indicate that the substance in question is selenium tetrachloride. The high values obtained in the analysis for selenium and the low ones for chlorine would be expected, both from the ease with which the tetrachloride absorbs water, with the loss of hydrochloric acid, and from the possible formation of a lower chloride of selenium. To eliminate this latter possible source of error, the precipitate was washed in some carefully dried carbon bisulphide, in which Ramsay and Evans[1] had found the lower chloride to be soluble, while the tetrachloride was insoluble. It was then analyzed by the much more satisfactory volumetric method of Fay and Norris.[2]

V. 0.2411 gram required the equivalent of 0.0856 gram Se or 35.5 per cent.

This result is in satisfactory agreement with the calculated

[1] J. Chem. Soc., 45, 65.
[2] This JOURNAL, 18, 703.

percentage composition of selenium tetrachloride, when the possible errors of the analysis are considered.

The reaction is practically a complete one, all the selenium being precipitated as tetrachloride. Nor does its vigor perceptibly decrease when the temperature is lowered to —20°. In spite too, of the fact that only infinitesimal amounts of water can be present as such, in either of the reagents, the reaction is apparently instantaneous.

Rose[1] discovered, long ago, that selenium tetrachloride is formed when selenates are heated with sodium chloride and sulphuric acid, chlorine being evolved, a reaction which is evidently somewhat analogous to the one here studied.

Cameron and Maccallan[2] also state that phosphorus pentachloride reacts violently with anhydrous selenic acid. It would not be surprising if selenium tetrachloride had also been formed here.

It is hoped to follow the course of the reaction between acetyl chloride and selenic acid more precisely, and to test its generality by substituting other halogens, especially fluorine, for chlorine.

The author wishes to thank Prof. A. Michael for his suggestion of, and assistance in, this research.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ESTERS OF SULPHURIC ACID AND OF CHLORSULPHONIC ACID.

By F. W. Bushong.

The secondary or neutral esters of sulphuric acid possess, as Nef[3] has shown, very low dissociation points. This explains the fact that it is impossible to obtain many of the homologous esters by the usual double decomposition method —interaction of dry silver sulphate with alkyl halides. Up to the present time only the methyl, ethyl, normal propyl, and isoamyl esters have been isolated. They have been found to act as alkylating agents.

[1] Pogg. Ann., 27, 575.
[2] Chem. News, 59, 233.
[3] Ann. Chem. (Liebig), 318, 40-50.

A further study of these and analogous compounds seems desirable, and the only possible method which presents itself for their synthesis at low temperatures is the interaction of sulphuryl chloride, Cl_2SO_2, or of chlorsulphonic esters, $Cl—SO_2—OR$, with the various free alcohols or their salts. The literature on this subject is rather conflicting and I have, therefore, taken up a careful study of these reactions, at the suggestion and under the guidance of Dr. Nef. My experiments are to be considered as preliminary, and it is the intention of Dr. Nef to continue further investigations in this direction.

Chlorsulphonic Ethyl Ester, $Cl—SO_2—OC_2H_5$.—This substance was first obtained, together with two others of the same empirical composition, by the union of sulphur trioxide with ethyl chloride.[1] Purgold proved it to be identical in its properties with the compound obtained in the interaction of potassium ethylsulphate and phosphorus pentachloride. Müller obtained the same compound, together with isethionic acid, by the addition of chlorsulphonic acid to ethylene.[2] It was also obtained by Sandmeyer[3] by the addition of ethyl hypochlorite to sulphur dioxide :

$$C_2H_5O—Cl + SO_2 \rightarrow Cl—SO_2—OC_2H_5.$$

Nef[4] has observed that chlorsulphonic ethyl ester is formed almost quantitatively by the interaction of free ethylsulphuric acid, which is now very easily accessible through Claesson's method,[5] and phosphorus pentachloride, the product being fractionally distilled under reduced pressure. This seemed, at first, the most practical method for isolating the compound under discussion. I have repeated Nef's experiments and analyzed the product obtained. It usually contains traces of oxychloride of phosphorus, which is removed by washing the oil repeatedly with water and subsequently drying it with cal-

[1] J. Chem. Soc., **19**, 100 (1857) ; Ann. Chem. (Liebig), **149**, 124 (1869) ; Ber. d. chem. Ges., **6**, 502 (1873).

[2] Ber. d. chem. Ges., **6**, 227 (1873).

[3] *Ibid.*, **19**, 860 (1886).

[4] Ann. Chem. (Liebig), **318**, 40 (1901).

[5] J. prakt. Chem., [2], **19**, 231 (1879).

cium chloride and then again distilling under reduced pressure.

I. 0.2257 gram substance gave, by the Carius method, 0.3695 gram $BaSO_4$.

II. 0.2666 gram substance required, after heating with lime, 19.24 cc. $AgNO_3$ solution (1 cc. = 0.00348 gram Cl) to precipitate AgCl, or gave 0.0669 gram Cl.

III. 0.2909 gram substance required 21.02 cc. $AgNO_3$ solution, or gave 0.0731 gram Cl.

	Calculated for $Cl—SO_2—OC_2H_5$.	Found. I.	II.	III.
S	22.18	22.48	....	....
Cl	24.52	....	25.09	25.14

Finally Behrend[1] prepared ethyl chlorsulphonate by the interaction of sulphuryl chloride and alcohol, according to the equation

$$Cl_2SO_2 + HOC_2H_5 \rightarrow HCl + Cl—SO_2—OC_2H_5.$$

Although Claesson[2] has shown that Behrend's work, in so far as it relates to the neutral esters of sulphuric acid, is unreliable, I have found that the following modification of Behrend's method yields ethyl chlorsulphonate to the extent of 60 per cent of the theoretical amount, and that the product is identical in its properties with that obtained by me from free ethylsulphuric acid and phosphorus pentachloride.

Sulphuryl chloride is brought into a distilling-flask, fitted with a doubly perforated stopper, through which are inserted the stem of a dropping-funnel and a glass tube drawn out to a capillary and extending below the surface of the acid chloride. The delivery-stem of the distilling-flask is connected with a wash-bottle containing water and then with an aspirator, and thus a steady stream of air, well dried with calcium chloride, is drawn through the apparatus. The distilling-flask is now immersed in a freezing-mixture of ice and salt, and absolute alcohol (a little in excess of 1 molecule) added drop by drop from the separatory-funnel. When all the alcohol has been added the freezing-mixture is removed, but the

[1] J. prakt. Chem. [2], 18, 28 (1877).
[2] *Loc. cit.*

air current kept up for half an hour, or until the solution acquires the room temperature and becomes perfectly colorless. The reaction-products now appear in two layers, which are separated. The lower one consists mainly of ethyl chlorsulphonate, and, after washing with cold water, drying with calcium chloride, and distilling once under reduced pressure, is practically pure. The upper layer, on distillation under reduced pressure, gives off much hydrochloric acid and yields only small amounts of diethyl sulphate and of ethyl chlorsulphonate. There is much charring.

The analysis of the product thus obtained (b. p. 52° under 14 mm. pressure) gave the following figures:

I. 0.3372 gram substance gave, by the Carius method, 0.5528 gram $BaSO_4$.

II. 0.4108 gram substance required, after heating with lime, 28.20 cc. $AgNO_3$ solution (1 cc. = 0.00349 gram Cl), or gave 0.0984 gram Cl.

III. 0.3450 gram substance required 23.53 cc. $AgNO_3$ solution, or gave 0.0821 gram Cl.

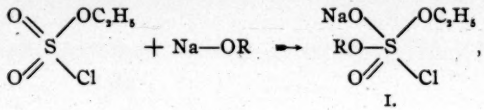
	Calculated for $Cl—SO_2—OC_2H_5$.	Found. I.	II.	III.
S	22.18	22.51	....	....
Cl	24.52	....	23.96	23.80

Ethyl chlorsulphonate, made by either of the methods just described, is a colorless, limpid liquid possessing a pungent odor and which irritates the eyes and excites tears. It boils at 52° under 14 mm. and at 58° under 20 mm. pressure. Its specific gravity was found to be 1.263 at 18° (Westphal). The substance is soluble in ligroin, chloroform, and ether, but attacks ether when warmed. It dissolves in fuming nitric acid and is precipitated unchanged by addition of water. Water affects it only slightly, even after standing with it for weeks in the cold. On heating, however, decomposition quickly sets in. Thus, 4.8 grams of the ester, heated in a distilling-flask containing 40 cc. of water (temperature of bath 125° to 130°), gave 130 cc. ethyl chloride or 16 per cent of the theoretical amount.

Claesson[1] has shown that ethyl chlorsulphonate is decomposed with violence in the cold by ethyl alcohol, giving varying quantities of ethyl ether, ethyl chloride, hydrogen chloride, ethylsulphuric acid, and diethyl sulphate (never over 20 per cent), and I have confirmed these observations.

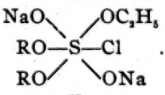
I. The Action of Chlorsulphonic Ethyl Ester on Sodium Alcoholates.

Sodium alcoholates (1.5 to 2 molecules), in ligroin or ethereal suspension, react with violence on the addition of ethyl chlorsulphonate. When absolute ether and only 1.5 molecules of the alcoholate are used, an almost clear solution results after some standing. This indicates the formation of an addition-product,



I.

and possibly also some ortho product,



II.

From the addition-product I., one would expect by subsequent loss of NaCl, the quantitative formation of a mixed ester of sulphuric acid, $RO—SO_2—OC_2H_5$. The facts are, however, as follows. There are always five reaction-products in varying proportions :

I. Alkyl ethylsulphate, $RO—SO_2—OC_2H_5$; the yield varies according as R is C_2H_5, C_5H_{11}, C_4H_9, or C_3H_7 from 37 to 62.2 per cent of the theory.

II. Alkyl sodium sulphate, $RO—SO_2—ONa$; 26 to 47.6 per cent according as R is C_2H_5, C_3H_7, C_4H_9, or C_5H_{11}.

III. A mixed ether, ROC_2H_5; determined as 27.7 per cent in one case only ($NaOC_2H_5$).

[1] J. prakt. Chem. [2], **19**, 231 (1879).

IV. Sodium sulphate; found to vary from 5 to 11 and 21.8 per cent, as the alcoholate used consisted of ethylate, isobutylate, or isoamylate.

V. Alcohol, ROH; not determined quantitatively and probably due to excess of alcoholate used.

From this it is evident that the reactions are very complicated, as is also the case when free ethyl alcohol acts on ethyl chlorsulphonate (see above). The formation of the mixed ether (III.) and of sodium alkyl sulphate (II.) cannot possibly be ascribed to the further action of the alcoholate on the neutral sulphate (I.) first formed,

$$RO—SO_2—OC_2H_5 + NaOR \rightarrow ROC_2H_5 + RO—SO_2—ONa,$$

as was proved by a special experiment using the ethylate and ethylsulphate, no action taking place at ordinary temperature after three hours standing in ligroin suspension. A complete explanation of these results cannot at this time be presented, as further experiments are necessary to decide between equally plausible theories. Suffice it to say at this point that various experiments show that ethyl chlorsulphonate (*e. g.*, behavior towards amines) is an energetic alkylating agent, which points to a ready dissociation of this compound into ethylidene[1] and chlorsulphonic acid,

$$\begin{matrix} \diagup \\ \diagdown \end{matrix} CH—CH_3 + Cl—SO_2—OH.$$

On this basis, for instance, the ether formation (III.) and formation of sodium alkyl sulphate (II.), as well as of sodium sulphate (IV.), can easily be understood.

Chlorsulphonic Ethyl Ester and Sodium Ethylate.—Twenty-five grams (2 mols.) freshly prepared sodium ethylate, dried at 180° in a hydrogen stream at reduced pressure, were suspended in 100 grams purified gasoline (b. p. 110° to 125°) and 25 grams ethyl chlorsulphonate slowly added by means of a dropping-funnel, during which operation the mixture was continually agitated and cooled by means of a freezing-mixture of ice and salt. The temperature of the solution was

[1] Ann. Chem. (Liebig), 318, 1–57 (1901).

then allowed to rise to about 10° and kept there until the odor of the acid ester had disappeared. The gasoline filtrate gave, after distillation by means of a Glinsky apparatus, 2.85 grams of ethyl ether, or 27.7 per cent of the theory. It has been proved by a special experiment that ether (3.62 grams) and gasoline (100 cc.) can very well be separated by fractional distillation (3.56 grams being recovered). The amount of diethyl sulphate, distilling between 96° at 18 mm. and 96° at 14 mm., obtained from the gasoline by fractional distillation under reduced pressure, was 9.92 grams, or 37.2 per cent of the theory. The salt residue, insoluble in gasoline, was now examined. It was dissolved in water and the solution then saturated with carbon dioxide and evaporated to dryness under reduced pressure. Digestion with absolute alcohol yielded 12.2 grams of sodium ethylsulphate, 47.6 per cent of the theory. The residue insoluble in alcohol gave, on dissolving in water, acidifying with hydrogen chloride, etc., 2.05 grams of barium sulphate, which corresponds to 1.25 grams of sodium sulphate, 5 per cent of the theory.

Ethyl Isoamyl Sulphate, $C_2H_5O—SO_2—OC_5H_{11}$.—Twenty-two grams (1.5 mols.) sodium isoamylate, dried at 220° in a hydrogen atmosphere at reduced pressure, were suspended in 100 cc. absolute ether and cooled in a freezing-mixture of ice and salt, and 19.5 grams ethyl chlorsulphonate added, drop by drop. The temperature of the reaction-mixture was now allowed to rise spontaneously to about 15°. It was observed that the sodium isoamylate gradually dissolved and that no salt separation took place after half an hour's standing at room temperature. On heating the mixture under a reversed condenser, much salt deposition took place. The ethereal filtrate was first distilled at about 100 to 150 mm. pressure in order to remove the excess of ether, and the amyl alcohol and amyl ethyl ether (a fair amount is present, but it was found impossible to separate it quantitatively from the amyl alcohol) formed in the experiment.

The residual oil was now distilled at about 18 mm. pressure. There was much charring and evolution of sulphur dioxide, but the distillate, after washing with dilute sodium

hydrate and drying with calcium chloride, yielded 5 grams, or 37 per cent of the theoretical amount, of pure ethyl isoamyl sulphate (see below). The salt residue, insoluble in ether, was worked up as in the ethyl series—*i. e.*, dissolved in water, saturated with carbon dioxide, etc. Absolute alcohol extracted 7.4 grams of sodium isoamyl sulphate,[1] or 29 per cent of the theory. The insoluble salt residue yielded 6.88 grams of barium sulphate, corresponding to 4.19 grams or 21.8 per cent sodium sulphate.

In a second experiment 34 grams of sodium isoamylate, 150 cc. ether, and 30 grams ethyl chlorsulphonate were used. The ethereal solution was not, however, heated under the reversed condenser. On adding about 25 grams of water a thick, gelatinous mass of salts was precipitated, which dissolved on addition of more water (125 cc.). The ethereal and aqueous solutions were now worked up as before. The oil that remained after the removal of the amyl alcohol and amyl ethyl ether was, however, not directly distilled, but first again taken up in ether, washed with dilute caustic alkali, dried with calcium chloride, and then distilled at reduced pressure. Thus 20 grams, or 49 per cent, of pure ethyl isoamyl sulphate were obtained.

0.4636 gram substance gave, by the Carius method, 0.5646 gram $BaSO_4$.

	Calculated for $C_2H_5O—SO_2—OC_5H_{11}$.	Found.
S	16.34	16.72

Ethyl isoamyl sulphate is a colorless oil resembling diethyl sulphate. Its odor is less agreeable, however, and reminds one of that of bananas. It boils at 127° to 128° under 15 mm. pressure, and possesses the sp. gr. 1.079 at 20° (Westphal). It is insoluble in, and not affected by, cold water, is readily soluble in alcohol, ether, and ligroïn. Heated to 140° it begins to decompose rapidly.

Ethyl Isobutyl Sulphate, $C_2H_5O—SO_2—OC_4H_9$.—Proceeding in a manner exactly like that described in the last experiment,

[1] It is assumed here, but not certain, that this salt is pure and free from sodium ethylsulphate. The same remark holds good of the corresponding salts obtained in the isopropyl and isobutyl series.

of the amyl series, 25 grams (1.5 mols.) sodium isobutylate, suspended in 100 cc. absolute ether, were treated with 30 grams of ethyl chlorsulphonate. The following reaction-products were isolated:

Ethyl isobutyl sulphate, 18.7 grams, or 50 per cent of the theory; sodium isobutyl sulphate, 9.6 grams, or 26 per cent of the theory; sodium sulphate, 3.2 grams, or 11 per cent of the theory.

The ethyl isobutyl sulphate obtained boils at 108° under a pressure of 13 mm. and possesses the sp. gr. 1.098 at 23° (Westphal). It is a colorless oil, insoluble in water, with an odor similar to that of mandrake.

0.6276 gram substance gave, by the Carius method, 0.8183 gram $BaSO_4$.

	Calculated for $C_4H_9O—SO_2—OC_4H_9$.	Found.
S	17.60	17.90

Ethyl Isopropyl Sulphate, $C_5H_{12}O—SO_2—OC_3H_7$.—The following results were obtained on treating 27 grams (2 mols.) sodium isopropylate, suspended in about 100 cc. ether, with 22.8 grams ethyl chlorsulphonate: Crude ethyl isopropyl sulphate, 16.2 grams, or 62.2 per cent; sodium isopropyl sulphate, 7.5 grams or 29.3 per cent of the theory. The ethyl isopropyl sulphate is much less stable than the other sulphates described, and consequently there is much loss in attempting to distil it even at reduced pressure. Its boiling-point is 105° at 18 mm. pressure, and the specific gravity at 21° was found to be 1.143 (Westphal). For the analysis, a distilled portion was taken up in ether, washed with dilute caustic soda, dried with calcium chloride, and then the ether removed by heating in a vacuum to 60°.

0.4904 gram substance gave, by the Carius method, 0.6664 gram $BaSO_4$.

	Calculated for $C_5H_{12}O—SO_2—OC_3H_7$.	Found.
S	18.95	18.65

The sodium isopropyl sulphate obtained closely resembles sodium isobutylsulphate in appearance, soapy feel, and solu-

bility in water and alcohol. A portion of it was hydrolyzed by means of hydrochloric acid and the alcohol thus obtained found to boil between 79°.5 to 82°. It gave acetone by oxidation as was proved by its conversion into indigo by condensation with *o*-nitrobenzaldehyde.

II. The Action of Sulphuryl Chloride on Sodium Alcoholates.

Since sulphuryl chloride and ethyl alcohol give over 60 per cent of the theoretical yield of ethyl chlorsulphonate, it is to be expected that sulphuryl chloride and sodium alcoholates (two or more molecules) will give results entirely analogous to those obtained above in the interaction of ethyl chlorsulphonate with sodium alcoholates, since alkyl chlorsulphonates must first be formed as intermediate products. This was found to be the case. There is, however, always in addition a formation of sulphite which, in the case of sodium isopropylate, amounted to 48.6 per cent of the theory. This can only be understood on the assumption that the dissociation-products[1] of sulphuryl chloride, *i. e.*, sulphur dioxide and chlorine, and not this reagent as such, act on the alcoholates.

Sulphuryl Chloride and Sodium Ethylate.—Thirty grams (3 mols.) of sodium ethylate, suspended in 100 grams of ligroin (b. p. 62° to 67°), were treated with 20 grams of sulphuryl chloride, proceeding in a manner entirely analogous to that described in the case of the ethyl chlorsulphonate. The odor of ethyl chlorsulphonate is at first very marked, and does not entirely disappear until the temperature reaches 15°. The ligroin filtrate yielded 6.5 grams, or 29.5 per cent of diethyl sulphate (b. p. 96° to 98°) at 15 mm. pressure. The salt residue was found to contain 11.8 grams, or 54 per cent, of sodium ethylsulphate (by extraction with alcohol after treatment in aqueous solution with carbon dioxide, etc.). It was also found to contain 0.73 gram of sodium sulphate (4.9 per cent) and 0.067 gram (or 0.7 per cent) sulphur dioxide, as determined by titration with N/10 iodine solution.

Diisoamyl Sulphate from Sulphuryl Chloride and Sodium Isoamylate.—Fifty-two grams (3.2 mols.) sodium isoamylate,

[1] Nef: Ann. Chem. (Liebig), 318, 40 (1901).

150 cc. absolute ether, and 20 grams of sulphuryl chloride gave 8 grams, or 23 per cent of diisoamyl sulphate,[1] b. p. 149° to 151° at 12 mm. pressure. The other products formed were not isolated.

Diisobutyl Sulphate, $(C_4H_9O)_2SO_2$. — Seventy grams of sodium isobutylate (3.25 mols.), suspended in absolute ether and treated with 30 grams of sulphuryl chloride, etc., gave 27.5 grams, or 55 per cent, of diisobutyl sulphate, b. p. 133° to 134° under 19 mm. pressure. For analysis the distillate was taken up in ether, washed with dilute caustic soda, dried with calcium chloride, and then the last traces of ether removed by heating in a distilling-flask from 60° to 80° at reduced pressure.

0.4308 gram substance gave, by the Carius method, 0.4848 gram $BaSO_4$.

	Calculated for $(C_4H_9O)_2SO_2$.	Found.
S	15.25	15.45

Diisobutyl sulphate cannot be prepared by the interaction of silver sulphate and isobutyl iodide.[2] As prepared above, its refractive index for sodium light was found to be 1.415, and the specific gravity is 1.042 at 23° (Westphal). The salt residue in the experiment described above was found to contain much sulphite (not determined quantitatively), and also yielded 6.6 grams, or 18 per cent, of sodium isobutyl sulphate, on digestion with alcohol.

Diisopropyl Sulphate, $(C_3H_7O)_2SO_2$.—Thirty-one grams (3.5 mols.) of sodium isopropylate, ether, and 15 grams of sulphuryl chloride gave 4.5 grams of crude diisopropyl sulphate, heated to 60° at reduced pressure, in a distilling-flask. The substance is very unstable,[3] undergoing decomposition on standing at ordinary temperature. On attempting to distil it at 18 mm. pressure, a small portion passed over at about 106°. For analysis the crude oil, not distilled, was taken up in ether, washed with caustic alkali, dried with calcium chlo-

[1] Nef: *Ibid.*, 318, 42 (1901).

[2] Ann. Chem. (Liebig), 318, 43 (1901).

[3] Berthelot has recently obtained this substance from propylene and sulphuric acid.

ride, and the ether removed by heating to 60° at reduced pressure. The substance evidently was not quite pure.

0.3454 gram substance gave, by the Carius method, 0.3956 gram $BaSO_4$.

	Calculated for $(C_3H_7O)_2SO_2$.	Found.
S	17.60	15.73

The salt residue in the experiment just described gave 18 grams, or 22 per cent, of sodium isopropyl sulphate on digestion with alcohol. The salt left, insoluble in alcohol, was found to contain 3.456 grams of sulphur dioxide (or 48.6 per cent) by titration with N/10 iodine solution.

III. The Action of Ethyl Chlorsulphonate upon Aniline.

This reaction has already been studied by Wenghöffer,[1] who obtained free sulphanilic acid as the only reaction-product. It is evident from the experiments of Wagner[2] and of W. Traube[3] and Bamberger[4] that phenylsulphaminic acid must first have been formed, which readily goes over into sulphanilic acid. It is noteworthy that no trace of an ester is formed according to the equation

$$C_6H_5NH_2 + Cl{-}SO_2OC_2H_5 \rightarrow C_6H_5NH{-}SO_2OC_2H_5 + HCl \rightarrow H_2NC_6H_4{-}SO_2OC_2H_5 + HCl,$$

as was proved by special experiments. Preliminary experiments with ethyl chlorsulphonate (1 mol.) and aniline (3 mols.) in ligroin solution have proved, furthermore, that much ethylaniline (in a free state as well as in form of the sulphate) is formed in this reaction, as was established by its conversion into ethylphenylnitrosamine.

These experiments, as well as the isolation of a mixed ether, ROC_2H_5, in the interaction of ethyl chlorsulphonate with free alcohols and their salts, show that ethyl chlorsulphonate is an alkylating agent, acting just as ethyl halides, nitrate, sulphate, etc.[5]

[1] J. prakt. Chem. [2], **31**, 1803.
[2] Ber. d. chem. Ges., **19**, 1157.
[3] *Ibid.*, **23**, 1653.
[4] *Ibid.*, **30**, 2275.
[5] Nef: Ann. Chem. (Liebig), **309**, 126–189; **318**, 1–40, 138–147.

I wish to cordially thank Dr. Nef for his careful guidance and cheerful help as well as for personal kindness shown during the prosecution of this work.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

THE ACTION OF CARBON MONOXIDE ON SODIUM ALCOHOLATES ALONE AND IN THE PRESENCE OF SALTS OF FATTY ACIDS.

By W. A. Beatty.

The synthesis of salts of fatty acids by the action of carbon monoxide on sodium alcoholates gives exceedingly poor yields and has been applied by Geuther and Fröhlich[1] with success only in two cases, namely, sodium methylate and ethylate.

The experiments of Nef[2] establish decisively that these syntheses take place in two stages: 1. The carbon monoxide absorbs the sodium hydroxide resulting from the dissociated sodium alcoholate molecules,

$$C_nH_{2n} + HONa \rightleftarrows C_nH_{2n+1}ONa,$$

and thus sodium formate,

$$O{=}C\rightleftarrows + H{-}ONa = O : C\begin{matrix} H \\ ONa \end{matrix},$$

is first formed. 2. The sodium formate is subsequently, and only to a very limited extent, absorbed by the alkylidene molecules simultaneously set free, as follows:

$$C_nH_{2n}\rightleftarrows + H{-}COONa = C_nH_{2n+1}COONa.$$

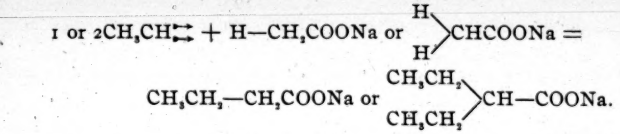
It is also clear from the experiments of Nef that the formation of alkylated fatty acids, which was observed by Geuther and his students on passing carbon monoxide over a mixture of a sodium alcoholate and a salt of a fatty acid, is an alkylation phenomenon.[3] The carbon monoxide unites with the sodium hydroxide coming from the dissociated sodium alco-

[1] Ann. Chem. (Liebig), **202**, 288–331.

[2] *Ibid.*, **318**, 185.

[3] *Ibid.*, **310**, 316–335; **318**, 143–172. Cf. *Ibid.*, **202**, 288–331; **218**, 57.

holate molecules to give sodium formate; the alkylidene molecules, liberated at the same time, then simply alkylate the fatty acid present,[1] *e. g.*:

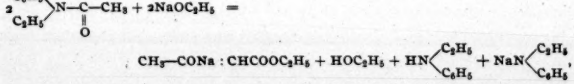


It seemed desirable, in view of the new interpretation of these syntheses, to repeat some of the experiments of Geuther and his students. I have therefore undertaken this work at the suggestion and under the direction of Dr. J. U. Nef.

The Action of Carbon Monoxide on Sodium Isoamylate.

This reaction has been studied by Geuther and Fröhlich,[2] who obtained much formic acid, some valeric acid, and an unsaturated acid, $C_{10}H_{18}O_2$, but no trace of isoamylformic acid. Geuther and his students used carbon monoxide made from yellow prussiate of potash and concentrated sulphuric acid, and there is some doubt whether every trace of air was excluded in their experiments. In fact it was sometimes found impossible to repeat or confirm their work. I shall, therefore, simply describe my own results and the exact conditions under which they were obtained, indicating and explaining briefly, wherever possible, the points not in accord with previous observations.

[1] Experiments carried out by Mr. Higley under my direction have now made it highly probable that at least some of these reactions proceed through an intermediate formation of acetoacetic ether. Thus ethylacetanilide (2 mols.) and sodium ethylate give, by aldol condensation (Ann. Chem. (Liebig), **298**, 319),



acetoacetic ether, which is thereupon converted, in part, into mono- and diethylated acetoacetic ether by the ethylidene molecules present. These substances then undergo the "acid splitting," and thus give rise to the mono- and dialkylated acetic acids obtained by Nef and by Geuther in their syntheses. Mr. Higley will soon publish his results in detail. J. U. Nef.

[2] Ann. Chem. (Liebig), **202**, 294.

The reaction-products obtained by me in the experiment under discussion were, besides valeric acid, 1, isopropylisoamylacetic acid; 2, decyl alcohol or isopropylisoamylethyl alcohol; 3, a lactone, $C_{11}H_{20}O_3$, or 1-isobutyl-2-isopropylbutyrolactone. As these substances had all been isolated and carefully studied by Nef in his experiments with sodium isoamylate my work was much simplified. It consisted in establishing rigidly the identity of the products obtained by me with the corresponding ones obtained by Nef. Furthermore, some time was spent in the study of an oxidation-product obtained from the lactone, $C_{11}H_{20}O_3$. A dibasic acid, *α*- or *trans*-isopropylisobutylsuccinic acid was thus obtained. This is isomeric—not identical—with a *β*- or *cis*-isopropylisobutylsuccinic acid obtained in two ways by synthesis, and up to the present time I have not been successful in converting one of these isomers into the other.

The carbon monoxide for all my experiments was prepared from oxalic acid and concentrated sulphuric acid. The carbon dioxide was removed from the gaseous mixture by means of washing-bottles containing concentrated caustic potash.

The carbon monoxide was collected in a gasometer and then purified and dried before use, as follows: It was first passed through two large Bunsen wash-bottles containing chromous chloride (to remove oxygen), and then through two tubes containing soda-lime and fused calcium chloride, and finally through a wash-bottle containing sulphuric acid.

The sodium isoamylate was prepared in the usual way, and the last traces of amyl alcohol were removed by heating in a bath at 220° under 20 to 30 mm. pressure. 450 grams of sodium isoamylate were heated in four large, glass tubes so placed in a sealed-tube furnace that the carbon monoxide had a continuous passage through the apparatus. The exit-tube was connected with an empty wash-bottle and then with a Schiff's azotometer. The rate of flow and absorption of gas could thus be roughly determined. Precautions were also taken to avoid an entrance of air when the furnace was turned off at

night by closing the end of the apparatus with a clamp and allowing the gas to flow at full pressure into the cooling tubes.

The sodium isoamylate was heated (temp. 180° to 190°) in a carbon monoxide atmosphere for about two weeks, seven hours daily. At the end of this time the tube contents were colored brown and some liquid had collected at the ends of the tubes. The mass was poured into much water and a larger amount of oil separated on top of the strongly alkaline aqueous solution. The neutral oils were extracted by means of ether and then dried with potassium carbonate. On distillation at reduced pressure, 12.2 grams of oil boiling between 60° and 100° under 60 mm. pressure (chiefly amyl alcohol) and 101.4 grams of oil boiling between 100° and 190° at 16 mm. pressure were obtained, besides 33 grams of resin left in the distilling-flask. The main fraction (101.4 grams) was now treated with a solution of 101.4 grams of caustic potash in twice its weight of alcohol, and heated with a return-condenser for ten hours, in order to saponify esters of acids and convert the lactone, $C_{11}H_{20}O_2$, into the corresponding γ-oxyundecylenic acid. The greater part of the alcohol was then distilled off and the residue treated with much water and extracted with ether. The ethereal extract, dried with potassium carbonate, gave, on distillation, 8 grams of oil (b. p. 130° to 208°), chiefly amyl alcohol and 25 grams of decyl alcohol boiling between 209° and 212°. Fourteen and seven-tenths grams of oil, boiling between 212° and 270°, were also obtained.

The decyl alcohol obtained was found to be identical with a decyl alcohol first observed by Borodin[1] and later by Guerbet.[2] Its constitution as isopropylisoamylethyl alcohol,

$$\begin{matrix}(CH_3)_2{-}CH \\ (CH_3)_2{=}CH{-}CH_2\end{matrix}\!\!\rangle CH{-}CH_2OH,$$

has been determined by Nef.[3] The identity was proved by converting it by means of potash-lime into the corresponding isopropylisoamylacetic acid (b. p. 241°) and its well-crystal-

[1] Ber. d. chem. Ges., 5, 480.
[2] Bull. soc. chim., 21, 450.
[3] Ann. Chem. (Liebig), 318, 151.

lized derivatives, the amide (m. p. 112°), and anilide (m. p. 105°). These were found to agree in all their properties with the corresponding substances obtained by Nef.

The alkaline solution resulting from the above-mentioned saponification yielded, on acidifying with diluted sulphuric acid and extracting with ether, a total of 31.6 grams of oily acids. On distillation at 9 mm. pressure, the following fractions were obtained: Six grams boiling between 90° and 125°; 5.7 grams between 125° and 130°; 12.7 grams between 135° and 137°; and 2 grams between 137° and 151°, leaving 5 grams of resin in the distilling-flask.

On redistillation and subsequent treatment of the higher boiling fractions with dilute soda, a small amount of oil was found to be neutral in character. It was therefore extracted by ether, and on fractionation yielded 4 grams of the γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$ (b. p. 141° to 145° at 10 mm. pressure). The soda solutions gave, on working up for acids, 3 grams of isovaleric acid (b. p. 174° to 176°) and 10 grams of isopropylisoamylacetic acid (b. p. 135° to 137° at 9 mm. pressure). The latter was, in part, converted into the crystallized amide and anilide mentioned above, and thus sharply identified.

The original alkaline solution was now worked up by acidifying with dilute sulphuric acid and extracting with ether. After drying with calcium chloride and driving off the ether the residual oil was distilled. Fifty and seventh-tenths grams of oil boiling up to 125° at 40 mm. pressure (chiefly formic and isovaleric acid) and 71.4 grams of oil boiling between 125° to 200° at 15 mm. pressure, were obtained, and 32 grams of resin were left in the distilling-flask. On treatment of the higher boiling fraction with soda a fair amount of oil was found to be neutral. It was therefore extracted by ether and yielded 10 grams of pure lactone, $C_{11}H_{20}O_2$ (b. p. 142° to 144° at 11 mm.). The soda solutions gave, on working up for acids, besides much isovaleric acid, 15 grams of pure isopropylisoamylacetic acid (b. p. 241°).

The lactone, $C_{11}H_{20}O_2$, obtained in this experiment was

identified by its conversion into the corresponding undecylenic acid and its crystalline amide[1] (m. p. 82°).

From the above it will be seen that 450 grams of sodium isoamylate yielded, after treatment with carbon monoxide for twelve days, 25 grams of decyl alcohol (isopropylisoamylethyl alcohol), 14 grams of γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$, 25 grams of isopropylisoamylacetic acid, besides some amyl alcohol and much formic and isovaleric acids.

The substances obtained in this experiment were sharply identified by conversion into well-known crystalline derivatives. Their analysis was deemed unnecessary because the same reaction-products were obtained in an experiment whose description follows and in which all the substances obtained were analyzed.

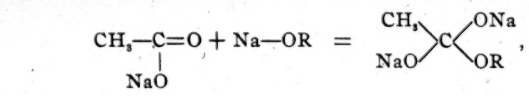
The Action of Carbon Monoxide on a Mixture of Sodium Acetate and Sodium Isoamylate.

By passing carbon monoxide over an equimolecular mixture of sodium ethylate and sodium acetate at 160° to 200°, Geuther and Fröhlich[2] obtained, among other products, ethylacetic acid and diethylacetic acid. By using a mixture of sodium isoamylate and sodium acetate Poetsch[3] isolated large amounts of an acid, $C_7H_{14}O_2$, which, from its properties, must be considered as isoamylacetic acid. Nef obtained[4] from sodium isoamylate and ethylacetanilide, at 150°, a large yield of isoamylacetic acid. These results are due either to a direct alkylation of the sodium acetate or ethylacetanilide present, or to an alkylation of an acetoacetic acid derivative (formed as an intermediate product through aldol condensation) and subsequent "acid splitting" of the mono- and dialkylated acetoacetic acid derivative—as pointed out in a foot-note in the introduction. It is also obvious that the oenanthylic acid, $C_7H_{14}O_2$ (b. p. 222° to 226°), obtained by Loos[5] by the action of sodium ethylate on sodium isovalerate must be identical with ethylisopropylacetic acid.

[1] Nef: Ann. Chem. (Liebig), **318**, 154–155.
[2] Ann. Chem. (Liebig), **203**, 288–331.
[3] *Ibid.*, **218**, 57.
[4] *Ibid.*, **318**, 145.
[5] *Ibid.*, **203**, 321.

Furthermore, Geuther and Fröhlich, as well as Poetsch, very frequently obtained in their experiments with sodium isoamylate neutral compounds which they regarded, without any further evidence, as ketones. It is obvious that one of these which was obtained by them in especially large amount and to which they give the boiling-point 203° to 210° was decyl alcohol, *i. e.*, the isopropylisoamylethyl alcohol mentioned above.

Finally, it is clear from what follows, that on mixing a sodium alcoholate with a sodium salt of a fatty acid (such as acetic or isovaleric acid) it is essential that the latter should be added, finely pulverized, directly to the alcoholic solution of the sodium alcoholate, and the alcohol subsequently removed by distillation in a hydrogen atmosphere at ordinary or reduced pressure. A more intimate mixture is thus obtained, and very probably a combination between the alcoholate and sodium salt of the fatty acid invariably takes place, *e. g.*,



and thus naturally an aldol condensation must take place by heat or on standing (even before the carbon monoxide is passed over the mixture). Such an addition-product was in fact isolated in the case of sodium ethylate and potassium acetate (see below).

Geuther and Fröhlich, as well as Loos and Poetsch, in the experiments alluded to, must have prepared their mixture of sodium alcoholate and sodium salt of a fatty acid in this way, for if one mixes intimately, in a mortar, dry sodium isoamylate and fused sodium acetate in equimolecular proportions, and then passes carbon monoxide over the mixture at 150° to 200°, the sodium acetate is left entirely unaffected. In this case the same reaction-products are obtained as when sodium isoamylate alone is used, as is evident from the following:

An equimolecular mixture, 310 grams, of sodium acetate and sodium isoamylate, obtained by grinding the two sub-

stances together in a mortar, was heated in the apparatus described above and carbon monoxide passed over it (temp. 180° to 200°) for eight days, seven hours daily. On working up as in the previous case—pouring into 4 liters of water, separating the neutral and acid components—the following products were obtained and sharply identified by conversion into well-defined and crystalline derivatives, and by analysis. The neutral portion gave, on the first fractionation, 25.7 grams of oil boiling from 70° to 90° at 60 mm., 14.5 grams boiling from 90° to 120° at 9 mm., and 18.9 grams oil boiling between 120° and 185° at 9 mm. pressure. Twenty-one grams of resin were left in the distilling-flask. The low-boiling oil was found to consist chiefly of isoamyl alcohol boiling from 129° to 131°. From the middle fraction, after two distillations, 9.1 grams of pure decyl alcohol boiling between 97° and 99° at 8 mm. pressure, were finally obtained. This was a fragrant oil that boiled at 210° to 212° and gave the following figures on analysis :

I. 0.2282 gram substance gave 0.6360 gram CO_2 and 0.2784 gram H_2O.

II. 0.1903 gram substance gave 0.5293 gram CO_2 and 0.2324 gram H_2O.

	Calculated for $C_{10}H_{22}O$.	Found. I.	II.
C	75.94	76.01	75.85
H	13.92	13.55	13.57

That the decyl alcohol obtained was isopropylisoamylethyl alcohol was proved by its conversion into isopropylisoamylacetic acid and its amide and anilide.

On refractionating the high-boiling neutral oil, 18.9 grams, two fractions were obtained and analyzed. The first of these boiled at 130° to 133° at 8 mm. and the second from 134° to 140° at the same pressure. No definite conclusion from the data obtained could be drawn concerning the nature of the product or products present.

It will be noticed that a similar product (14.7 grams, b. p. 212° to 270°) was obtained in the first experiment with sodium isoamylate and carbon monoxide alone (see above).

It is probable that some 1,3-decylglycol (α-isobutyl-β-isopropyltrimethyleneglycol),[1] as well as some amyl decylate and decylvalerate, were present, but I was unable to establish this rigidly by experiment. The high-boiling fractions were digested with alcoholic potash and thus 3 grams of decyl alcohol and 2 grams of a neutral oil (b. p. 132° to 136° at 10 mm. pressure), which gave no definite results on analysis, were obtained. The alkaline solution resulting from the saponification gave, on working up for acids, 3 grams of isovaleric acid (b. p. 174° to 176°) and 4.5 grams of oil boiling from 140° to 142° at 10 mm. pressure. The latter was found to be neutral towards soda and to consist chiefly of γ-oxyundecylenic acid lactone, $C_{11}H_{20}O_2$.

From the original alkaline solution, containing the acid reaction-products, 50 grams of crude, oily acids were isolated. On distillation, the following fractions were obtained: 9 grams boiling up to 60° at 60 mm. pressure; 8.9 grams boiling from 60° to 100° at 20 mm.; 20.6 grams boiling from 100° to 180° at 20 mm. pressure. Ten grams of resin remained in the distilling-flask. On treating the higher-boiling fraction with soda and extracting with ether, 10 grams of the lactone, $C_{11}H_{20}O_2$, boiling from 141° to 143° at 12 mm. pressure, were obtained.

I. 0.2120 gram substance gave 0.5566 gram CO_2 and 0.2028 gram H_2O.

II. 0.1176 gram substance gave 0.3091 gram CO_2 and 0.1139 gram H_2O.

	Calculated for $C_{11}H_{20}O_2$.	Found. I.	Found. II.
C	71.74	71.6	71.68
H	10.87	10.62	10.77

The lactone was also identified through conversion (4 grams) into the lime salt, which was crystallized from much water and dried at 100°.[2]

0.5108 gram salt gave 0.1578 gram $CaSO_4$.

	Calculated for $C_{22}H_{38}O_4Ca$.	Found.
Ca	9.05	9.08

[1] Ann. Chem. (Liebig), 318, 165.

[2] Cf. Nef: *Loc. cit.*

The remainder of the lactone was converted into the corresponding undecylenic acid and its amide, m. p. 82°, and these were found to be identical in their properties with those given by Nef.

The soda solutions from which the lactone had been removed and the lower-boiling fractions, mentioned above, were found to contain chiefly two acids, much isovaleric acid (b. p. 175°), and about 15 grams of isopropylisoamylacetic acid (b. p. 241°), proved by conversion into the amide (m. p. 112°) and the anilide (m. p. 105°). The intermediate fraction, 2 grams only, may have contained traces of isoamylacetic acid, which boils at 212°, but it is certain that this substance is not an essential reaction-product in the experiment carried out as described above. Poetsch obtained, in a similar experiment from 746 grams of sodium isoamylate and 546 grams of sodium acetate, 40 grams of decyl alcohol (b. p. 203° to 206°), 50 grams of isovaleric acid (b. p. 165° to 200°), 80 grams of isoamylacetic acid (b. p. 200° to 240°, chiefly 212° to 213°), and 40 grams of acid boiling from 240° to 300° (isopropylisoamylacetic acid(?), lactone, $C_{11}H_{20}O_2$(?)). The cause of the difference in the results obtained has already been discussed.

The formation of a primary decyl alcohol, its corresponding isopropylisoamylacetic acid, and a lactone, $C_{11}H_{20}O_2$, by the action of carbon monoxide on sodium isoamylate alone or in the presence of sodium acetate, as shown above, is easily understood in view of the experiments of Nef.[1]

Valeraldehyde, which is formed by the action of isoamylidene on sodium hydroxide, is alkylated by the excess of isoamylidene molecules present and thus isopropylisoamylacetaldehyde,

$$(CH_3)_2CH-\underset{\displaystyle H}{\underset{|}{CH}}-CH:O + \rightleftarrows CH-CH_2CH(CH_3)_2 =$$

$$(CH_3)_2CH-\underset{\displaystyle (CH_3)_2CHCH_2CH_2}{\underset{|}{CH}}-CHO,$$

is first formed, which is then in part reduced by the atomic

[1] Ann. Chem. (Liebig), **318**, 147–173.

hydrogen present to the corresponding decyl alcohol, and in part converted by the sodium hydroxide, according to the Dumas-Stas' reaction, into isopropylisoamylacetic acid.

The valeraldehyde is also in part converted into the aldol which by reduction gives 1-isobutyl-2-isopropyltrimethyleneglycol. The 1,3-decylglycol,[1] or its monosodium salt thus formed, then reacts by alkylation with the sodium formate (resulting from the action of carbon monoxide on sodium hydroxide) to give the oxy-acid, $C_{11}H_{22}O_3$, which, on acidifying, goes over spontaneously into the lactone, $C_{11}H_{20}O_2$.

$$(CH_3)_2CH-\underset{|}{CH}-CH_2OH$$
$$(CH_3)_2CH-CH_2-C\rightleftarrows + H-COONa + H_2O \text{ or } NaOH =$$

Dissociated 1,3-decylglycol.

$$(CH_3)_2CH-\underset{|}{CH}-CH_2OH$$
$$(CH_3)_2CH-CH_2-\underset{|}{CH}-COONa.$$

Na salt of the oxy-acid $C_{11}H_{22}O_3$.

The interaction between carbon monoxide and sodium isoamylate is thus in every way analogous and comparable to that taking place between sodium isoamylate and formethylaniline which has been exhaustively investigated by Nef.

The Oxidation of the Lactone $C_{11}H_{20}O_2$ to α- or Trans-isopropylisobutylsuccinic Acid, $(CH_3)_2CH-\underset{|}{CH}-COOH$ / $(CH_3)_2CH-CH_2-\underset{|}{CH}-COOH$.

The constitution of the lactone, $C_{11}H_{20}O_2$, as given above, follows from the fact that the corresponding oxy-acid, $C_{11}H_{22}O_3$, gives by oxidation with permanganate, or by treatment with potash-lime at 250°, a dicarboxylated acid, $C_9H_{16}=(COOH)_2$. This proves that the hydroxyl group in the oxy-acid must be present as a primary alcohol group, and

[1] Rosinger claims (Ann. Chem. (Liebig), 322, 131–133) that the substance described by me (Ann. Chem. (Liebig), 318, 165) was not 1,3-decylglycol but its monovalerate. This is incorrect, as my substance was heated for two hours with an excess of caustic potash at 110° and I obtained 39 grams of isovaleric acid from 201.4 grams valeraldehyde taken. Furthermore, I expressly state (p. 166) that my decylglycol was not affected by alcoholic potash. In his experiments, Rosinger has determined clearly the conditions under which the monovalerate of 1,3-decylglycol can be isolated as an intermediate product. J. U. Nef.

consequently excludes another possible formula for the oxy-acid, *e. g.*:

$$(CH_3)_2CH-\underset{\displaystyle (CH_3)_2CH-CH_2-\underset{|}{C}HOH}{\overset{\displaystyle CH-CH_2}{|}} + H-COONa + H_2O \text{ or}$$

Dissociated 1,3-decylglycol.

$$NaOH = (CH_3)_2CH-\underset{\displaystyle (CH_3)_2CH-CH_2-\underset{|}{C}HOH}{\overset{\displaystyle CH-CH_2-COONa}{|}}$$

Sodium salt of a γ-oxy-acid, $C_{11}H_{21}O_3$.

An oxy-acid of the constitution given here would be readily oxidized to a γ-ketonic acid or to a secondary amylisobutyl-ketone but could not possibly give a dibasic acid, $C_{11}H_{20}O_4$, with the same number of carbon atoms—hence the constitution of the lactone, $C_{11}H_{20}O_2$, as given by Nef, must be correct.

Twenty grams of lactone, $C_{11}H_{20}O_2$, prepared according to Nef's method, were heated with a concentrated solution of caustic soda until the lactone had all dissolved. On cooling, a solution of 20 grams of potassium permanganate was added at once and the mixture (volume about 1 liter) allowed to stand in the cold until decolorized. After filtering, acidifying, extracting with ether, the oily reaction-product obtained was distilled at reduced pressure. Six grams of lactone, $C_{11}H_{20}O_2$, were recovered and the residue left in the distilling-flask (bath 200° at 9 mm.) solidified on cooling. It was washed with low-boiling ligroin and then crystallized from hot water, and thus about 12 grams of an acid, crystallizing in long needles and melting at 142°, were obtained.

0.2041 gram substance gave 0.4580 gram CO_2 and 0.1702 gram H_2O.

	Calculated for $C_{11}H_{20}O_4$.	Found.
C	61.10	61.19
H	9.26	9.26

A silver salt was made by adding a solution of the acid, carefully neutralized by means of dilute ammonia, to an excess of aqueous silver nitrate. The salt comes down as a white, flocculent precipitate, which was well washed and dried over sulphuric acid *in vacuo*.

0.2218 gram salt gave, on ignition, 0.1110 gram Ag.

	Calculated for $C_{11}H_{18}O_4Ag_2$.	Found.
Ag	50.23	50.00

The *α*- or *trans*-isopropylisobutylsuccinic acid thus obtained is easily soluble in ether and alcohol, but almost insoluble in benzene and ligroin. A very small amount (0.1 gram) of a lower melting (109° to 115°) acid was found in the aqueous mother-liquors, but it was impossible to determine the nature of this product. It certainly is not isopropylsuccinic acid or the *β*- or *cis*-isopropylisobutylsuccinic acid obtained by synthesis (see below).

α- or *trans*-Isopropylisobutylsuccinic acid is also obtained in fine yield by heating the lactone $C_{11}H_{20}O_2$, with an excess of potash-lime at 250° until the evolution of hydrogen ceases. Thus, 6 grams of lactone gave 5 grams of oily-acid products from which 2.5 grams of the pure acid, melting at 142°, were obtained.

Synthesis of β- or cis-Isopropylisobutylsuccinic Acid,

$$(CH_3)_2CH-CH-COOH$$
$$\quad\quad\quad

must be concluded that the latter is the *trans* modification. Up to the present time I have not been successful in converting these isomers into each other, although it must be admitted that neither of them has yet been exhaustively studied, and only one experiment was carried out in this direction. Heated in a sealed tube with concentrated hydrochloric acid at 200° to 230° the *cis*, as well as the *trans*, isomer was recovered unaltered.

The *cis*-isopropylisbutylsuccinic acid, which melts at 118° to 119°, was prepared, in two ways, synthetically:

1. From sodium isobutylmalonic ester and α-bromisovaleric ester. The resulting isopropylisobutylethane tricarboxylate,

$$(CH_3)_2CH-CH_2-C(COOC_2H_5)_2$$
$$\qquad\qquad\qquad\qquad |$$
$$(CH_3)_2=CH-CHCOOC_2H_5,$$

saponified by means of alcoholic potash, gave, by subsequent loss of carbon dioxide, the substance under discussion.

2. From α-bromisobutylacetic ether and sodium malonic ester. The resulting isobutylethanetricarboxylate,

$$(CH_3)_2CH-CH_2-CH-COOC_2H_5$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\quad HC(COOC_2H_5)_2,$$

was then converted into sodium salt, and this, treated with isopropyliodide, gives an isomeric isopropylisobutylethane tricarboxylate, which, on saponification and loss of carbon dioxide, gives *cis*-isopropylisobutylsuccinic acid.

First Method of Synthesis.—Eighty-three grams of isobutylmalonic ester were converted into the sodium salt by treatment in absolute ethereal solution with sodium wire. The sodium salt is very soluble in ether and is obtained, on removing the ether over sulphuric acid *in vacuo*, as a gelatinous, sticky mass. This was treated in sealed tubes with the theoretical amount of ethyl α-bromisovalerate, heating at first for six hours at 125° to 130° and then for eight hours at 140° to 150°. On pouring into water, extracting with ether, and fractionating *in vacuo*, 36 grams of isopropylisobutylethane tricarboxylate,[1] boiling at 175° to 180° at 14 mm. pressure,

[1] Cf. Bischoff: Ber. d. chem. Ges., 29, 976.

were obtained (there was a considerable forerunner). Heated for eight hours under a reversed condenser with 30 grams of caustic potash and 60 grams of alcohol, saponification took place, and the corresponding free acid was obtained as an oil, on extracting the acidified solution with ether. On heating to 240° it lost carbon dioxide and gave the anhydride of *cis*-isopropylisobutylsuccinic acid. It was dissolved in concentrated aqueous caustic potash. On acidifying, extracting with ether, etc., the crude acid obtained gradually solidified while standing over sulphuric acid *in vacuo*. It was now washed with low-boiling ligroin and purified by dissolving in glacial acetic acid and precipitating by addition of water. *cis*-Isopropylisobutylsuccinic acid is thus obtained in white, crystalline needles or plates, melting at 118° to 119°. The acid, which is quite soluble in acetone, acetic ether, benzene, and acetic acid, but very sparingly soluble in cold water, was not analyzed in the free state. It gives insoluble calcium and silver salts (analysis, see below). Especially characteristic is its behavior towards ammonia after heating to 240°, when anhydride formation probably takes place (the anhydride was not isolated). On addition of aqueous ammonia, solution takes place and on acidifying with sulphuric acid a very voluminous, white precipitate separates out. This is the amino acid,

$$C_9H_{15}\begin{cases}CONH_2\\COOH\end{cases}.$$

It was purified by dissolving in acetone and precipitating with water. It formed fine, silky needles, melting at 145° to 146° (analysis, see second method of synthesis).

In a similar manner the corresponding anilido and *p*-toluido acids were obtained, *i. e.*, by treating the heated *cis*-acid with aniline and *p*-toluidine, respectively. The former melts at 149° to 150° (needles, from alcohol) and the latter at 156° to 157°.

The calcium salt of *cis*-isopropyllsobutylsuccinic acid, obtained as a crystalline precipitate on adding a solution of the acid, carefully neutralized with ammonia, to concentrated,

aqueous calcium chloride, gave the following analytical results, after drying at 140°.

I. 0.3700 gram salt gave 0.0812 gram CaO.

II. 0.2208 gram salt gave 0.0481 gram CaO.

	Calculated for $CaC_{11}H_{18}O_4$.	Found. I.	Found. II.
Ca	15.75	15.67	15.55

The corresponding silver salt, made by double decomposition from the ammonium salt and silver nitrate, was obtained as a white, amorphous precipitate.

0.4160 gram salt, dried over H_2SO_4 *in vacuo*, gave 0.2080 gram Ag.

	Calculated for $C_{11}H_{18}O_4Ag_2$.	Found.
Ag	50.23	50.19

The silver salt of the amino acid, $C_9H_{18}\begin{cases}CONH_2\\COOH\end{cases}$, melting-point 146°, was obtained by double decomposition reaction from the ammonium salt and silver nitrate as a white, gelatinous, amorphous precipitate.

0.2767 gram salt, dried over sulphuric acid *in vacuo*, gave 0.0949 gram Ag.

	Calculated for $C_{11}H_{20}O_3NAg$.	Found.
Ag	33.54	33.7

Second Method of Synthesis.—Isobutylacetic acid (b. p. 200° to 202°), made according to the directions of W. A. Noyes,[1] was converted into α-bromisobutylacetic ether (b. p. 99° to 102° at 17 mm. pressure), by the method of Bentley and Perkin.[2] One hundred and forty-two grams of the α-brom-ester were treated in sealed tubes with 56 grams of sodium malonic ester, heating first for five hours at 100° and then for sixteen hours at 135° to 140°. Thus 130 grams of α,α,β-iso-hexane tricarboxylate,

$$(CH_3)_2CH-CH_2-\underset{\displaystyle CH(COOC_2H_5)_2}{\overset{\displaystyle |}{CH}}COOC_2H_5,$$

[1] J. Am. Chem. Soc., 18, 393.

[2] J. Chem. Soc. (London), 73, 49.

(b. p. 176° to 177° at 19 mm. pressure) were obtained.

0.2421 gram substance gave 0.5298 gram CO_2 and 0.1877 gram H_2O.

	Calculated for $C_{18}H_{32}O_4$.	Found.
C	59.80	59.71
H	8.55	8.62

A portion of the substance (10 grams) was saponified by means of alcoholic potash and converted by subsequent loss of carbon dioxide into isobutylsuccinic acid, which was found identical in its properties with those given in the literature. Another portion, 40 grams, was converted into the sodium salt by means of sodium in absolute ethereal solution. The salt, which is quite soluble in ether, is obtained on evaporation of the ether over sulphuric acid in a vacuum as an amorphous mass. It was heated in a sealed tube with 1.5 molecules of isopropyliodide, at first for two hours at 125° and then for ten hours at 140° to 150°. On working up the reaction-product, 20 grams of oil (b. p. 186° to 188° at 15 mm. pressure) were obtained. Analysis proved that the product was still not quite completely alkylated.

0.2094 gram substance gave 0.4772 gram CO_2 and 0.1721 gram H_2O.

	Calculated for $C_{18}H_{32}O_4$.	Found.
C	62.8	62.01
H	9.3	9.18

The substance was, therefore, again treated with sodium and isopropyl iodide. A product, boiling from 188° to 190° at 15 mm. pressure, was now obtained which is obviously pure isopropylisobutylethane tricarboxylate,

$$(CH_3)_2CH—CH_2—CHCOOC_2H_5$$
$$\qquad\qquad\qquad\quad |$$
$$(CH_3)_2{=}CH—C(COOC_2H_5)_2.$$

It was saponified with alcoholic potash and the resulting oily acid converted by heating to 240° with loss of carbon dioxide into the anhydride of *cis*-isopropylisobutylsuccinic acid. On adding aqueous ammonia and acidifying, the amino acid,

mentioned above, separates out as a bulky precipitate. It was purified by dissolving in acetone and precipitating with ligroin. Fine needles, melting at 146°, and identical in all their properties with the corresponding product in the first method of synthesis, were obtained. The substance is soluble in alcohol and acetone, very slightly soluble in ether and chloroform, and practically insoluble in benzene and ligroin. Heated with lime or with concentrated aqueous potash, it gives off ammonia and is converted into *cis*-isopropylisobutylsuccinic acid melting at 118°. An analysis of the amino acid (an analysis of the silver salt is given above) gave the following results:

0.2163 gram substance gave 0.4868 gram CO_2 and 0.1937 gram H_2O.

0.2500 gram substance, heated with lime, required 11.5 cc. N/10 H_2SO_4 on titration.

	Calculated for $C_{11}H_{21}NO_2$.	Found.
C	61.39	61.35
H	9.76	9.95
N	6.51	6.44

Sodium Ethylate and Sodium Acetate Heated Alone and in the Presence of Carbon Monoxide.

A repetition of the experiment by Geuther and Fröhlich,[1] using a mixture of 380 grams of sodium ethylate and sodium acetate (equal molecules mixed intimately in a mortar) and passing carbon monoxide over the mass at 180° to 200° for four days of seven hours each, gave, besides 2 grams of a neutral oil and much formic and acetic acids, only 2 grams of a solid acid, melting from 165° to 172°, which could not be identified as mesitylenic acid. Two grams of normal butyric acid, boiling from 160° to 175°, were also obtained.

The following experiment proves that butyric acid is formed by simply heating the mixture of the acetate and ethylate, *i. e.*,

[1] *Loc. cit.*

without passing carbon monoxide over it: Two hundred and ninety grams of sodium ethylate and sodium acetate (equal molecules mixed intimately in a mortar) were heated for five days, of seven hours each, to 200° to 210°. No neutral products were found and 4 grams of butyric acid, boiling from 160° to 164°, were obtained. A portion of this was converted into the calcium salt and analyzed.

0.3727 gram salt gave 0.2376 gram $CaSO_4$.

	Calculated for $CaC_8H_{14}O_4$.	Found.
Ca	18.68	18.75

Besides this, 2 grams of acid boiling from 165° to 195° were obtained, which probably contains some diethylacetic acid. No solid acid was obtained in this experiment.

It is likely that much more decisive results would have been obtained by adding 1 molecule of sodium acetate to an alcoholic solution of sodium ethylate. Subsequent removal of the alcohol in an atmosphere of hydrogen, at 200° to 210°, etc., must result in a partial or even complete interaction between the two ingredients. The following experiment makes this exceedingly probable: On mixing alcoholic solutions of sodium ethylate and potassium acetate, a very voluminous precipitate separates out at once in the cold. This is probably the ortho addition-product,[1] $CH_3—C(ONa)(OK)(OC_2H_5)$, corresponding to Claisen's orthobenzoic acid derivatives,[2] $C_6H_5—C(OR)(OR')(ONa)$.

The Dissociation of Sodium Methylate.

One hundred grams of alcohol-free sodium methylate, prepared in the usual way, were heated in a distilling-flask in a bath, the temperature of which ranged from 260° to 400° during the course of the experiment. The distilling-flask was connected with a short condenser, an empty Bunsen wash-

[1] This product is now being investigated in the laboratory. J. U. Nef.

[2] Ber. d. chem. Ges., 20, 649.

bottle with two tubes containing bromine and a gasometer. No olefine bromides were obtained. Fifteen liters of gas, proved by analysis to consist of 90 per cent hydrogen and 10 per cent marsh-gas, were obtained. The strongly-charred residue left in the distilling-flask was found to give off acetylene with water, as proved by its conversion into the silver and copper salt. Three liters of gas were thus obtained, which was found by analysis to consist of 30 per cent hydrogen and 70 per cent acetylene.

The residue left in the distilling-flask after treatment with water consisted of free carbon and sodium carbonates. The proportion was found to be 12 grams of combined carbon to 8.5 grams of free carbon.

The formation of acetylene in small quantities, on treating the salt residue with water, proves that sodium acetylene, C_2Na_2, is one of the decomposition-products of sodium methylate by heat. This can readily be understood in view of the experiments of Nef.[1] Formaldehyde (or its addition-product $H_2C(ONa)_2$), which is formed by the interaction of the dissociation-products of sodium methylate, *i. e.*, of methylene with sodium hydroxide,

$$CH_2 \rightleftarrows + 2H{-}ONa = CH_2(ONa)_2 + 2H,$$

gives, by dissociation, atomic carbon,

$$CH_2O \text{ or } CH_2(ONa)_2 = C \text{ and } H_2O \text{ or } 2NaOH.$$

The atomic carbon acts in part on the sodium hydroxide present to give free sodium, but in great part polymerizes to graphite and amorphous carbon. In this operation diatomic carbon,[2] C=C, is naturally first formed which unites in part with the sodium set free to give disodium acetylene,

[1] Cf. Ann. Chem. (Liebig), **298**, 303: **318**, 189 and 197. The marked physiological properties of aqueous formaldehyde solutions is due to the presence of atomic carbon particles formed by dissociation, $H_2C(OH)_2 \rightleftarrows H_2O + \begin{matrix} H \\ OH \end{matrix}\!\!>\!C \rightleftarrows 2H_2O + C$, as has been pointed out by Nef in his lectures on organic chemistry for some years past.

[2] The formation of calcium carbide and of acetylene in the electric furnace or arc, respectively, is due to a partial dissociation of the graphite or amorphous carbon, C_x, into diatomic carbon, $C_x \rightleftarrows \frac{x}{2}(C:C)$, which then unites at once with the calcium or hydrogen atoms present to form calcium carbide or acetylene, respectively. J. U. NEF.

$$C_2 + Na_2 = C_2Na_2.$$

In conclusion, I desire to thank Dr. Nef for the assistance and encouragement he has given me in the course of my work.

REVIEWS.

NOTES ON METALLURGICAL ANALYSIS. Arranged for Students of Metallurgical Chemistry. Selected Methods for the Analysis of Iron and Steel, and of the Materials used in Their Manufacture, Including the Analysis of Gases, Fuels, Water for Boiler Supply, etc., together with Explanatory Notes on the Manipulation and Chemistry of the Various Processes. By NATHANIEL WRIGHT LORD, E.M., Professor of Metallurgy and Mineralogy at the Ohio State University, and Consulting Chemist of the Ohio Geological Survey. Second edition, rewritten, and greatly enlarged. Columbus, Ohio, 1903, Metallurgical Laboratory, Ohio State University.

The promise on the long title-page is fulfilled in the text. The student, who has worked through the analytical methods given, should be well qualified for practical work. Professor Lord explains and criticizes all of the familiar standard methods as well as many of the newer methods, and gives abundant literature references. He assumes in the student a knowledge of inorganic chemistry and qualitative analysis and some knowledge of quantitative analysis, and in the 222 pages of text no space is wasted on descriptions of reagents and common apparatus, as is so common in books on metallurgical chemistry. Professor Lord's work is so good that it should find frequent use. E. R.

ANALYTICAL CHEMISTRY. By F. P. TREADWELL, PH.D., Professor of Analytical Chemistry in the Polytechnic Institute of Zurich. Translated with the author's permission from the second German edition by WILLIAM T. HALL, S.B., Instructor in Chemistry, Massachusetts Institute of Technology. Volume I. Qualitative Analysis. First edition, first thousand. New York: John Wiley & Sons. 1903. pp. 463. Price, $3.00.

Professor Treadwell is widely known as a good chemist, teacher, and lecturer. This book is, as he says in the preface, "a somewhat amplified repetition" of his lectures on analytical chemistry. It is well written, interesting, well translated by Mr. Hall, and its appearance is creditable to the publishers. Of modern innovations, the author utilizes the law of mass action, the theory of electrolytic dissociation and hydrolysis, explaining their relations to analysis, and making special reference throughout the book in those places where these laws serve to made dark places clear.

The book will be a pleasant addition to a chemical library,

and will doubtless be helpful and suggestive to students, but it is not necessary for them, for lectures in qualitative analysis involve much repetition and review of general chemistry, and only the most important analytical methods can be mentioned in such a course of lectures. So this book contains little which is not to be found in the larger text-books of chemistry, supplemented by the average laboratory manual, but it is too large, handsome, and costly to use in the laboratory, while the analytical methods given are too few for it to be used as a reference book. Nor can it supplant a text-book, for there is no mention of argon or helium, for example, the author very properly confining himself to those elements and compounds which occur in the ordinary scheme of instruction in qualitative analysis. E. R.

ANLEITUNG ZUR UNTERSUCHUNG DER FÜR DIE ZUCKERINDUSTRIE IN BETRACHT KOMMENDEN ROHMATERIALIEN, PRODUKTE, NEBENPRODUKTE, UND HILFSSUBSTANZEN. Sechste umgearbeitete und vermehrte Auflage. Herausgegeben von PROF. DR. R. FRÜHLING. Braunschweig: Friedrich Vieweg und Sohn.

This work of Dr. R. Frühling, of Braunschweig, has now reached its sixth edition. The book contains 505 pages, and treats in general of the chemistry of materials entering into the manufacture of beet sugar.

The first part is devoted to descriptions of the apparatus used in the optical and chemical analysis of sugar juice, sugars, molasses, sugar beets, limestones, water, and the other substances necessary to the manufacture of sugar from the sugar beet. The methods of analysis of these bodies are also given in sufficient detail. The rules for the analysis of sugar, adopted by the International Committee for the Unification of Sugar Analysis, which met in Paris in 1900, are also given.

This is the first edition of the work which discusses in full the necessity of polarizing sugar solutions at a standard temperature, or of correcting the polarizations if the temperatures differ from the standard. Both the method of Wiley and Schönrock are given, but the author fails to distinguish the different principles on which the correction factors of the two methods are ascertained. In the method of Wiley it is directed that the solutions be made up and polarized at the same temperature, while in the method of Schönrock it is directed that they be made up at the standard temperature and the correction is for a polarization at a different temperature.

The latest and best forms of polariscopic apparatus are described. The method of determining sugars in mixtures is given and elaborate tables for use in the chemical determina-

tion of sugars by the reduction of alkaline copper solutions are furnished. The various methods of ascertaining the richness of sugar beets designed for seed production are described.

An interesting feature of the work is the space it devotes to the residues of sugar manufactories, especially the disposal of the molasses. The increasing importance of molasses as a cattle food is recognized by a description of the methods of analyses of foods into which molasses enters. The growing importance of the sugar industry in the United States demands that works of this kind be placed at the disposal of chemists and engineers in order that the processes of manufacture may be conducted according to the most improved methods and with the greatest economy.

Dr. Frühling has devoted the greater part of his active life to the study of these problems, and this, the latest and largest edition of his work, will commend itself to all who are interested in the sugar industry. H. W. W.

AN INTRODUCTION TO THE STUDY OF THE COMPOUNDS OF CARBON OR ORGANIC CHEMISTRY. By IRA REMSEN, President of the Johns Hopkins University. Fourth revision. Boston: D. C. Heath & Co. 1903.

"The important advances that have been made in the field of organic chemistry during the past few years have made a thorough revision of this book necessary. The present edition gives the results of the revision. The principal changes and additions will be found in the chapters dealing with the sugars, stereoisomerism, the diazo compounds, and the terpenes. The treatment of the aromatic compounds is, in general, fuller than in the older editions. Although considerable has been added, the size of the volume has not been markedly increased, the difference between the last edition and the present being only about 50 pages. In addition to the changes indicated above, minor changes have been made throughout, and the author believes that the book is now fully in harmony with the present state of organic chemistry."—[Preface to the Fourth Revision.]